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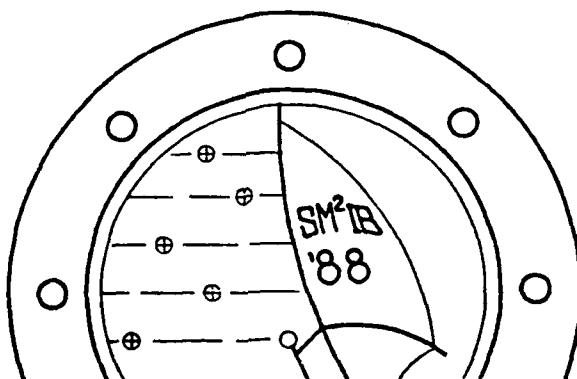
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INTERNATIONAL CONFERENCE
ON SURFACE MODIFICATION OF METALS
BY ION BEAMS

RIVA DEL GARDA, ITALY
12-16 SEPTEMBER 1988

FINAL PROGRAM
AND
ABSTRACTS



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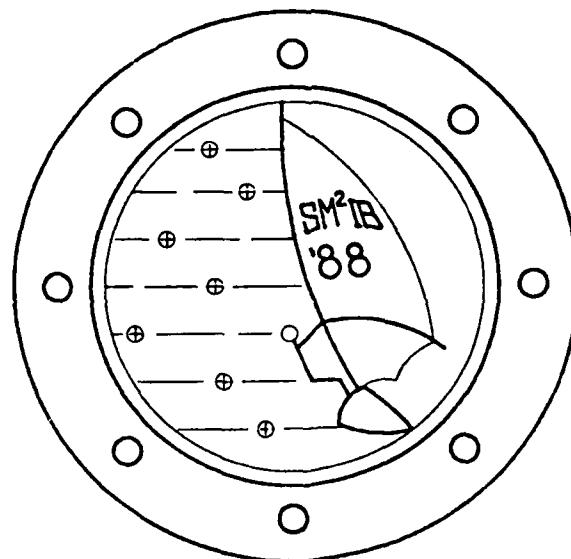
I. R. S. T. - UNIVERSITY OF TRENTO

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SM²IB CONFERENCE SERIES

MANCHESTER, U.K, 1975

MANCHESTER, U.K, 1978

MANCHESTER, U.K, 1981

HEIDELBERG, FRG, 1984

KINGSTON, Canada, 1986

RIVA DEL GARDA, Italy, 1988

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SUPPORTING ORGANIZATIONS

The conference is supported by the Institute for Scientific and Technological Research (IRST, a branch of ITC -Istituto Trentino di Cultura-Trento, Italy), the Physics Department and the Engineering Department of Trento University, Italy, and the Italian National Research Council (CNR). The Commission of the European Communities (Directorate General for Science, Research and Development), the University of Kingston in Canada (which was host to the previous SM²IB Conference), the Metallurgical Society of AIME, USA, and the U.S. Army Research, Development and Standardization Group UK, have also generously supported the Conference.

SPONSORS

The following firms have financially supported the Conference.

Acciaierie di Bolzano (Italy)	Banca di Trento e Bolzano (Italy)
Cameca (France)	Cenfor (Italy)
Circuiti Stampati CST, (Italy)	Danfysik (Denmark)
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GKN Bound Brook Italia (Italy)	IBM Italia (Italy)
Italstructures (Italy)	Spire Corporation (USA)
Tecvac (UK)	

REGISTRATION

The registration desk will be open at the Palazzo dei Congressi in Riva del Garda on Sunday September 11, 1988, from 3 p.m. to 8 p.m. and on Monday, September 12, from 8 a.m. to noon. For the remainder of the Conference, the Secretariat Office will be open during the Conference works.

SESSIONS

- A) Fundamentals of surface modification by ion beams. High dose ion implantation.
- B) Ion induced surface phases. Amorphization, interface mixing, quasi-crystalline structures, phase transformations.
- C) Modification of mechanical properties (wear, fatigue, hardness, adhesion,...).
- D) Mechanisms and applications of ion beam assisted deposition.
- E) Modification of chemical, electrochemical and oxidation properties.
- F) Thin film metallurgy for microelectronic applications.
- G) Industrial applications of ion beam techniques. Methods and equipments.

CONFERENCE SESSIONS AND PROCEEDINGS

The conference has oral and poster presentations, all of which are held in the Palazzo dei Congressi of Riva del Garda. For details of the Conference schedule, please see the attached Program.

Poster presentation

Posters presented in Session I may be mounted starting on Monday morning, September 12, and have to be removed by Tuesday evening. Posters in Session II may be mounted starting late on Tuesday and may remain in place until noon on Friday. The panel area allotted for each poster is 2 m by 2 m. Authors are requested to stay by their posters during the Poster Sessions.

Oral presentations

The time available for a contributed paper is 20 minutes (40 minutes for an invited paper), including 3 (5) minutes for answering questions from the audience. Please, do not exceed these times.

Proceedings

Publication of the papers will be made in Materials Science and Engineering. The publisher, Elsevier Sequoia, will compile a hard-cover volume of the proceedings, which will be sent after the conference to all fully paid registrants of the Conference.

EXHIBITION

During the Conference an exhibition of equipment and services for surface modification and related areas will be held. The exhibiting firms include:

Cenfor (Italy)
Danfysik (Denmark)
Implant Sciences Corporation (USA)
Instruments SA Italia (Italy)
Italstructures (Italy)
Tech-ni-plant (UK)
Whickam (UK)

The exhibition is located immediately outside the Conference rooms. Coffee breaks take place near the exhibition booths.

SPOUSES PROGRAM

Riva del Garda is located in a very interesting region, rich in artistic, natural and historic monuments. The material found in the Conference package gives you some information about the attractions of this area. In addition you could take advantage of the Travel Agency Desk available during the Conference in the Palazzo dei Congressi and of the various trips offered.

SOCIAL ACTIVITIES

The Social Activities include:

- i) The welcome reception on Sunday, September 11, at 7.30 p.m. in the Palazzo dei Congressi;
- ii) The excursion on Wednesday, Sept. 14, in the afternoon. Some buses will take us to a beautiful sightseeing point, to some characteristic and impressive geologic features, to a spectacular waterfall. The detailed program will be announced on Wednesday morning, also on the basis of the weather conditions.
- iii) The Conference final banquet, which will be offered free of charge to all participants on Thursday, September 15, starting at 7.45 p.m. (meeting point in front of the Palazzo dei Congressi).

SM²IB'88

CONFERENCE PROGRAM

MONDAY 12

09:30 WELCOME ADDRESS

10:00 **W.A. Grant Plenary Lecture**
«William A. Grant and the Beginnings of Surface Modification», H. Hermann, Univ. of Stony Brook, USA

10:40 COFFEE BREAK

SESSION A Fundamentals

Chairmen: R. Kelly and P. Mazzoldi

11:20 A-1 Invited
«Transport Processes in Solids During Ion Implantation», P. Mazzoldi, Univ. of Padova, Italy and A. Miotello, Univ. of Trento, Italy.

12:00 A-2
«Temperature and Dose Dependence of N implantation into Fe: Experimental Results and Numerical Modelisation», G. Terwagne, M. Piette and F. Bodart, LARN and ISIS, Belgium, and W. Moller, MPI für Plasmaphysik, FRG

12:20 A-3
«Surface precipitations of Ion Implanted Li and B in Metals», D. Fink, Hahn Meitner Inst., FRG

12:40 A-4
«Dissolution and Reprecipitation of Nitride Precipitates in Carbon Steel by Low Dose alpha-particle bombardment», S.M.M. Ramos, L. Amaral, M. Behar, A. Vasquez, G. Marest and F.C. Zawislak, Brasil

13:00 BREAK

15:00 A-5 Invited
«Composition Changes with Bombarded Alloys», R. Kelly, IBM Research Center, USA

15:40 A-6
«X-ray Studies of Noble Gas Inclusions in Aluminium Single Crystals», L. Graabæk and J. Bohr, RISO Ntl. Laboratory, Denmark; E. Johnson, H.H. Andersen, A. Johansen and L. Sarholt-Kristensen, Oersted Institute, Denmark.

16:00 A-7
«Dynamic Mixing and its Application in Improving the Interface Adhesion», W.Z. Li, L. Yi, F.Z. Cui and H.D. Li, Tsinghua Univ., China

16:20 **POSTER SESSION I**
(see enclosed detailed poster session program)
AND COFFEE BREAK

SESSION B Ion Induced Phases

Chairman: C. Tosello

18:00 B-1 Invited
«Temperature Effects on Ion Implanted Microstructure», D.I. Potter, C.H. Koch and J.K. Steele, Metallurgy Dept., Univ. of Connecticut, USA

TUESDAY 13

SESSION B (Cont.) Ion Induced Phases

Chairmen: J.L. Whitton and P.M. Ossi

08:30 B-2 Invited
«Experimental and Theoretical Developments in Ion Beam Induced Amorphization», P.M. Ossi, CESNEF, Milano, Italy

09:10 B-3
«Surface Metallurgy with High Energy Heavy Ion Beams», M.Z. Vasconcellos, S.R. Teixeira, P.H. Dionisio, W.H. Schreiner, and I.J.R. Baumvol, UFRGS, Brasil

09:30 B-4
«Phase Formation During Ion-Beam Mixing of Transition-Metal Multilayers», L-U. A. Andersen, J. Bottiger, K. Dyrbye, K. Pampus, and R. Poulsen, Univ. of Aarhus, Denmark

09:50 B-5
«Mixing and Annealing Effects in the Kr-irradiated Fe-Pd System», G. Battaglin, S. Lo Russo, and G. Principi, Univ. of Padova, Italy

10:10 B-6
«Detailed Analysis of the Amorphization Process in Ion-bombarded Metallic Alloys», L. Thomé, A. Benyagoub, and F. Pons, CSNSM, Orsay, France, E. Ligeon, J. Fontenille, and R. Danielou, Grenoble, France

10:30 COFFEE BREAK

11:00 B-7
«Amorphization Process in Mn-implanted Al Thin Films and Single Crystals: Effects of Strains and Target Temperature», A. Seidel, S. Massing, B. Strehlau, and G. Linker, KFZ, Karlsruhe, FRG

11:20 B-8
«Temperature Dependence of Amorphization and Precipitation Processes in Ni^+ and N^+ -implanted Ni_3Ti Alloys», J. Delage, O. Popoola, J.P. Villain, and P. Moine, Poitiers, France

SESSION C Modification of Mechanical Properties

Chairmen: E. Ramous, I. Baumvol and F. Zuliani

11:40 C-1 Invited
«Phase Transformations of a N-implanted Austenitic Stainless Steel (X10 CrNiTi 189)», R. Leutenecker, Fraunhofer Institut, Munich, FRG, and G. Wagner, T. Louis, and U. Gonser, Univ. Saarland, FRG, L. Guzman, and A. Molinari, Trento, Italy

12:20 C-2
«MeV N-implantation in Fe and Ti: a Microstructure and Hardness Study», A.M. Vredenberg, F.Z. Cui, and F.W. Saris, FOM, Amsterdam, The Netherlands

12:40 C-3
«A Fundamental Study of Titanium Nitride Films Deposited by Ion Beam Mixing», K. Hayashi, K. Sugiyama, K. Fukutani, and H. Kittaka, Nippon Steel Corp., Japan

13:00 BREAK

15:00 C-4 Invited
 «Ion Implantation in Ceramics», C.J. McHargue, Oak Ridge Ntl. Laboratory, USA

15:40 C-5
 «Ion Implantation and Fatigue Crack Initiation. Interaction of Persistent Slip Bands with Modified Surface Layers», D.S. Grummon, Michigan State Univ. East Lansing, USA; D.J. Morrison, J.W. Jones, and G.S. Was, The Univ. of Michigan, Ann Arbor, USA

16:00 C-6 -
 «Ion Beam Modification of Solid Lubricants on Metals», N.J. Mikkelsen and G. Sorensen, Inst. of Physics, Univ. of Aarhus, Denmark

16:20 C-7
 «Effects of Oxide Layer on the Friction and Wear of Ti-implanted Steels», I.L. Singer, NRL, USA; R.A. Jeffries, Geo-Centers, Inc. MD, USA

16:40 C-8
 «Effect of Ion Implantation on Fatigue and Freitling of Ti-6Al-4V», R.P.M. Procter, S. Sarias and W.A. Grant, Corrosion and Protection Center, UMIST, Manchester, U.K. and Univ. of Salford, U.K.

17:00 **POSTER SESSION I (Cont.)**
 (see enclosed detailed poster session program)
AND COFFEE BREAK

SESSION C (Cont.)

17:40 C-9
 «Structural Characterization and Fatigue Behaviour of a Carbon-implanted Pure Crystalline Nickel», S. Patu M.H. Xu and Z.G. Wang, Inst. of Metal Research, China

18:00 C-10
 «Examinations of Wear, Hardness and Friction of N, B, C, Ag, Pb, and Sn-implanted Steels with Different Chromium Contents», A. Kluge, K. Langguth, R. Ochsner, K. Kobs and H. Ryssel, Fraunhofer-Arbeitsgruppe für Integrierte Schaltungen, Erlangen; and Philips Forschungslaboratorium Hamburg, FRG

18:20 C-11 Invited
 «Ion Implantation in Japan in Non Semiconductor Fields», M. Iwaki, RIKEN, Saitama, Japan

WEDNESDAY 14

SESSION D

Ion Beam Assisted Deposition

Chairmen: P.G. George and G.K. Hubler

08:30 D-1 Invited
«Fundamentals of Ion Beam Assisted Deposition: Technique and Film Properties», G.K. Hubler, N.R.L., Washington, USA

09:10 D-2
«Simultaneous Ion Implantation and Deposition», J.P. Budinavicius, L.J. Pranavicius, S.J. Tamulevicius and J.J. Vosylius, Kaunas Polytechnic Institute, Lithuanian S.S.R., USSR

09:30 D-3
«The Effect of Ionization in Producing Large Intermix Layers in Ion Plating», R.F. Hochman and W.B. Carter, Georgia Institute of Technology, Atlanta, USA

09:50 D-4
«Surface Modification of Structural Materials by Dynamic Ion Mixing Process», S. Nakashima, M. Fukushima, M. Hagiwara, Hitachi Research Laboratory; I. Hashimoto, Kobuku Works, Hitachi; and K. Terakado, Sawa Works, Hitachi, Japan

10:10 D-5
«HPIB-Induced Melting and Mixing in Deposited Structures», A. D. Pogrebnyak and G.E. Remnev, Nuclear Physics Institute, Tomsk, USSR

10:30 **POSTER SESSION II**
(see enclosed detailed poster session program)
AND COFFEE BREAK

SESSION D (Cont.)

12:20 D-6 Invited
«New Compounds Synthesis by Ion Assisted Deposition (emphasizing the High T_c Superconductors)», J.J. Cuomo, IBM T.J. Watson Research Center, Yorktown Heights, N.Y., USA

13:00 BREAK

14:00 Afternoon Excursion

THURSDAY 15

SESSION E

Modification of Oxidation and of Corrosion Properties

Chairmen: P.L. Bonora, G.K. Wolf and P.G. Orsini

08:30 E-1 Invited
«Ion Beam Assisted Coatings for Corrosion Studies», W. Ensinger and G.K. Wolf, Universität Heidelberg, FRG

09:10 E-2
«Effect of Reactive Element Ion-Implantation on the High Temperature Oxidation of Ni-25 Cr», P.Y. Hou, Lawrence Berkeley Laboratory, Berkeley, USA; J. Stringer, Electric Power Research Institute, Palo Alto, USA

09:30 E-3
«Surface Oxidation of Cu Observed by PAC and RBS», A. Bartos, W. Bolse, K.P. Lieb and M. Uhrmacher, II. Physikalisches Inst. der Univ. Göttingen and Sonderforschungsbereich 126, Clausthal/Göttingen, FRG

09:50 E-4
«Effect of Ce Implantation on the Corrosion of Alloy 800H in S-O-C Environments», M.F. Stroosnijder, J.F. Norton, V. Guttmann, Joint Research Centre Petten, The Netherlands; M.J. Bennett, AERE Harwell, England; and J.H.W. de Wit, Delft University of Technology, The Netherlands

10:10 E-5
«Electrocatalytic Properties of Ion Implanted Oxide Films», L. Elifenthal, J.W. Schultze, Universität Düsseldorf, FRG; O. Meyer, KFZ Karlsruhe, FRG

10:30 E-6
«Localized Corrosion Behaviour of Al Surface Alloys Produced by Ion Beam Mixing and Ion Implantation», P.M. Natishan, E. Mc Cafferty and G.K. Hubler, Naval Research Laboratory USA.

10:50 **POSTER SESSION II (Cont.)**
(see enclosed detailed poster session program)
AND COFFEE BREAK

SESSION E (cont.)

11:40 E-7 Invited
«Improved High Temperature Oxidation Behaviour of Alloys by Ion Implantation», M.J. Bennett, D.J. Chivers, M.R. Houlton and A.T. Tuson, Materials Development and Nuclear Physics Divisions, Harwell Laboratory, England

12:20 E-8
«Corrosion Studies of Refractory Metals in Hot Acids by Ion Beam Techniques», W. Ensinger and G.K. Wolf, Physikalisch-Chemisches Institut der Universität Heidelberg, FRG

12:40 E-9
«Electrochemical and Corrosion Behaviour of BN Coated Aluminium Alloys Surface», L. Fedrizzi, M. Elena, S. Gialanella, M. Dapor and L. Guzman, IRST and University of Trento, Italy

13:00 BREAK

SESSION C (Cont.)
Modification of Mechanical Properties

Chairman: R.P.M. Procter

15:00 C-12 Invited
«Ion Implantation in China in the Non Semiconductor Field», G.L. Zhang, Institute of Low Energy Nuclear Physics, Beijing Normal University, China

SESSION F
Thin Film Metallurgy for Microelectronics

Chairman: G. Soncini

15:40 F-1 Invited
«The Current Status of Metallization in Integrated Circuits Applications», R.J. Holwill, Dept. of Electrical Engineering, Univ. of Edinburgh, Scotland

16:20 F-2
«Metallizations Used in Integrated Circuits and Ion Beam Effects», G. Ottaviani, Università di Modena, Italy

16:40 COFFEE BREAK

17:10 F-3
«A Metal Vapor Plasma System for Thin Film Metallurgy», P. W. Kidd, TRW Space and Defense, Redondo Beach, California, USA

17:30 F-4
«Properties of Oxide and Nitride Layers in Aluminium Produced by High Dose Ion Implantation», S. Ohira, NIKKEI Techno Research, Shizuoka, Japan; M. Iwaki, RIKEN, Saitama, Japan

17:50 F-5
«Ar Ion Beam Effect upon Photoemissive Thin Films», P. Dolizy and F. Grolière, Laboratoires d'Electronique et de Physique Appliquée, Philips Research Organ., Limeil Brévannes, France

19:45 Banquet

FRIDAY 16

SESSION G Equipment and Industrial Applications

Chairmen: G. Della Mea and J. K. Hirvonen

08:30 G-1 Invited
«Ion Beam Processing for Industrial Applications», J.K. Hirvonen, Spire Corporation, Bedford, USA

09:10 G-2
«Improvement in Friction and Wear of Hard Chromium Layers by Ion Implantation», W. Lohmann, Enka AG, Obernburg, FRG; J.G.P. van Valkenhoef, Akzo Materials and Corrosion Engineering, Hengelo Ov, The Netherlands

09:30 G-3
«Ion Implantation in WC-Co: Analysis of Treated Surfaces and Testing of Industrial Tools», L. Guzman, L. Ciaghi, F. Giacomozi, E. Voltolini, IRST, Povo (Trento), Italy; G. Dearnaley, P. Gardner and A. Peacock, AERE Harwell, England

09:50 G-4
«A Universal High Current Implanter for Surface Modification of Materials», B.R. Nielsen, P. Abrahamsen and S. Eriksen, Danfysik A/S, Denmark

10:10 COFFEE BREAK

10:40 G-5 Invited
«Plasma Source Ion Implantation, a new Approach to Ion Beam Modification of Materials», J.R. Conrad, Dept. of Nuclear Engineering and Engineering Physics, University of Wisconsin, USA

11:20 Panel Discussion
«Industrial Applications of Ion Implantation Techniques».

13:00 END OF SESSIONS

POSTER SESSIONS
DETAILED PROGRAM

POSTER SESSION I

A. Fundamentals
B. Ion Induced Phases
C. Modification of Mechanical Properties

A-8 «Titanium Implantations into a High Speed Steel Distribution Parameters and CEMS Characterization», M.A. Elkahani, H. Jaffreziec, G. Marest, N. Moncoffre and J. Tousset, Institut de Physique Nucléaire de Lyon, Université Claude Bernard LYON I, France

A-9 «Nuclear Resonance Analysis Depth Profiling of Na Implanted into Al and AISI 316 Ti-Steel», M. Uhrmacher, A. Kehrel, N. Scapellato, and K.P. Lieb, Univ. Göttingen, FRG

A-10 «Calculation of Ion Implants Depth Profiles at High Dose», A.J. Armini, and S.N. Bunker, Implant Sciences Corp., Danvers, USA

A-11 «Sputtering of Copper Crystals by Soluble/Nonsoluble Metal Ions», L. Sarholt-Kristensen, A. Johansen, and E. Johnson, Ørsted Institute, Denmark; N. Chechenin, Moscow State Univ., USSR

A-12 «In Situ Study of Surface Deformation Fields Induced by Ion Implantation», L. Augulis, B. Jasulionis, I. Pozela, L. Pranevicius, Kaunas Polytechnic Inst. Lithuania, USSR

A-13 «Ion Induced Surface Modifications of Co Crystals», A. Johansen, E. Johnson, and L. Sarholt-Kristensen, Ørsted Institute, Denmark; V.S. Chemyshev, Moscow State Univ., USSR

B-9 «Target Temperature Dependence on Ti Oxide Formation by High Dose Oxygen Implantation into Ti Sheets», Y. Okabe, Saitama Inst. of Tech., Japan; M. Iwaki, and K. Takahashi, RIKEN, Saitama, Japan

B-10 «TEM Study of Amorphization and Precipitation in Ni⁺ Implanted Aluminum», M.F. Denanot, O. Popoola and P. Moine, Lab. de Metallurgie Physique, Poitiers, France

B-11 «Influence of Ion Beam Irradiation on the Superconducting and Structural Properties of the High T_C Oxides Thin Films», B. Egner, J. Geerk, H.C. Linker, O. Meyer, J. Remmel, B. Strehlau, F. Weschenfelder, G.C. Xiong, KFZ Karlsruhe, FRG

B-12 «Solid Rare Gas Bubbles in Metals Probed by Mössbauer Nuclei», H. Pattyn, J. Oderus and S. Bukshpan, Univ. of Leuven, Belgium

B-13 «Surface Deformations by High Dose MeV Energy: He, Ne, and Ar Ions», F. Paszti, Central Res. Inst. for Physics, Budapest, Hungary

B-14 «TEM Study of the Microstructures of Ion Implanted Steels», G. J. Cai, Z. Q. Jin, Y. R. Chen, Southwest Jiaotong Univ., Sichuan, China; G. L. Zhang, Beijing Normal University, China.

B-15 «Different Crystalline Structures of Ru-rich Metastable Phases Formed by Ion Beam Mixing of the Binary Systems Ag-Ru and Au-Ru», M. Buchgeister, W. Hiller, K. Kopitzki, G. Mertler and E. Peiner, Univ. Bonn, FRG; W. Jäger, KFA Jülich, FRG

B-16 «Ion Beam Mixing of Selected Binary Metal Systems with Large Positive Heats of Formation», W. Hiller, M. Buchgeister, K. Kopitzki and E. Peiner, Univ. Bonn, FRG

B-17 «Glancing Angle X-ray Diffraction and SEM Studies of N₂⁺ Implanted Tantalum», R.M. Raole, RSIC, IIT, Bombay, India; A.M. Narsale, D.C. Kothari, P.S. Pawar, S.V. Gogawale, Univ. of Bombay, India; L. Guzman and M. Dapor, IRST, Trento, Italy

B-18 «Ion Beam Effects on Fe-Ni Bilayers», L. Gratton, C. Tosello, Univ. of Trento, Italy; S. Lo Russo and G. Principi, Univ. of Padova, Italy; W. Keune, Duisburg University, FRG; J. Parellada, Univ. of Barcelona, Spain

C-13 «Characterization of Transfer Films on Oxidized Ti-Implanted Steel», S. Fayeulle and J.L. Singer, Naval Research Laboratory, Washington DC, USA

C-14 «TEM Investigation of Structural Transformations in Ti, TiAl after N, C, B Implantations and Friction», J.C. Pivin, P. Zheng and M.O. Ruault, CSNSM, Orsay, France

C-15 «Friction and Wear Measurements of Oxidized Titanium Surfaces Bombarded With Ion Beams in the Hundred keV Region», B.M. Lund, N.J. Mikelsen, L. M. Schmidt and G. Sorensen, University of Aarhus, Denmark

C-16 «MeV Ion Beam Polishing of Anodically Grown Alumina», B. Daudin and P. Martin, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Grenoble, France

C-17 «Dislocation Structures in Near Surface Layers of Pure Metals Formed by Ion Implantation», A. N. Didenko, A.I. Rjabchikov, G.P. Isaev and N.M. Arzubov, Nuclear Physics Institute, Tomsk, USSR; Y.P. Sharkeev, E.V. Kozlov, G.V. Pushkareva and I.V. Nikonova, Institute of Civil Engineering, Tomsk, USSR, and A.E. Ligachev, Inst. of Aircraft Technology, Moscow, USSR

C-18 «The Influence of Temperature on The Performance of Ion Implanted Metal-Forming Tools», Chr. Weist, Inst. für Umformtechnik, Stuttgart, FRG and P. Ballhause, G.K. Wolf, Physikalisch-Chemisches Institut der Universität Heidelberg, FRG

C-19 «Effect of HPIB Bombardment on Structure and Properties of TN-20 and VK-8 Alloys», A.D. Pogrebnyak, G.E. Remnev, V.P. Janovskii, Inst. of Nuclear Physics, Tomsk, USSR and R.D. Babajanov, A. Emiraliiev, Inst. of Applied Physics, Tashkent State University, USSR

C-20 «Mechanical Property Changes in Ion Implanted Silicon Nitride for Rolling Element Bearings», A.J. Armini, Implant Sciences Corporation, Danvers, USA and J.A. Morrison, Rolls-Royce Inc., Atlanta, GA, USA

C-21 «Increased Microhardness, Wear Resistance and Corrosion Resistance of HPIB-irradiated Alloys», A.E. Ligachev, V.P. Nesterenko, A.V. Nesmelev, M.S. Opekunov, A.D. Pogrebnyak, I.F. Isakov, G.E. Remnev, V.S. Ukhonov, N.I. Shabanov, I.B. Kurakin and V.B. Kushnarenko, Institute of Aircraft Technology, Moscow, USSR

C-22 «Microhardness, Artificial Ageing and Fatigue Behaviour of Nitrogen Implanted Alloy Steel», J. Lunarski, W. Zielecki, Rzeszow Technical University, Poland; G. Gawlik, J. Jagielski and A. Podgorki, Institute for Electronic Material's Technology, Warsaw, Poland

C-23 «Wear Resistance Improvement and Structural Modifications of B⁺ Implanted Austenitic Stainless Steel», S. Raud, H. Garem, J.P. Villain and P. Moine, Lab. de Métallurgie Physique, Poitiers, France

C-24 «The Effect of Ion Beam Surface Modifications on Fatigue Crack Initiation in Polycrystalline Nickel», D.J. Morrison, J.W. Jones, D.E. Alexander, C. Kovach, and G.S. Was, University of Michigan, USA

C-25 «Microstructure and Mechanical Properties of High Dose Nitrogen Implanted Metals», T. Fujihana, T. Sugasawa, Advanced Technology Inc, Yokohama, N. Matsuzawa, Y. Okabe, Saitama Institute of Technology, M. Iwaki, RIKEN, Japan

C-26 «Annealing Behaviour of Nitrogen Ion Implanted 304 Stainless Steel», Sadhna Shrivastava, Ram D. Tarey, Amitabh Jain and K. L. Chopra, Indian Institute of Technology, New Delhi, India

C-27 «Nitrogen Ion Implantation into Intermetallic Compound Ti₃Al», K. Saito and T. Matsushima, National Research Institute for Metal, Tsukuba Lab, Ibaraki, Japan

C-28 «Post Implantation Heat Treatment of Nitrogen Implanted 440C Stainless Steel», Pao Huang and Robert F. Hochman, Georgia Institute of Technology, Atlanta, GA

C-29 «Mechanical Properties of CuNi and FeAl Films Produced by Dynamic Ion Mixing», J.P. Riviere, S. Pimbert, C. Sarrazin, J. Delafond, Université de Poitiers, France, and J. Von Stebut, Ecole des Mines de Nancy, France

POSTER SESSION II

D. Ion Beam Assisted Deposition
E. Modification of Oxidation and of Corrosion Properties
F. Thin Film Metallurgy for Microelectronics
G. Equipment and Industrial Applications

D-7 «Nitrogenation of Metal Surfaces by Ar⁺ Ion Bombardment», Y. Baba and T.A. Sasaki, Japan Atomic Energy Research Institute, Japan

D-8 «Structure and Properties of TiC Grown by Dynamical Ion Beam Mixing», S. Pimbert-Michaix, C. Chabrol, UNIR-EC, France; M.F. Denanot, and J. Delafond, Lab. de Métallurgie Physique, Poitiers, France

D-9 «Mixing of Metallic Multilayers with Light Ions», A. Traverse, CSNSM, Orsay, France; L. Nérot, B. Pardo and C. Corno, Inst. d'Optique, Orsay, France

D-10 «Physical Properties of Ti_xN Thin Films», A. Cavallari, M. Dapor, F. Giacomozzi, S. Girardi and F. Marchetti, IRST, Trento, Italy

D-11 «Formation of the Alloys by Ion Beam Mixing in the Temperature Range 300-600 K», R. Brenier, P. Thévenard, A. Perez, J. Rivory, M. Treilleux, Université Claude Bernard - LYON I, France

D-12 «Radiation Enhanced Diffusion in Ion Bombarded Ag/Ni Thin Film Multilayers», D. Marton, J. Fine, and G.P. Chambers, National Bureau of Standards, USA

D-13 «Ion Impact Induced Diffusion: New Evidence for a Complex Defect Mechanism», D. Marton and J. Fine, National Bureau of Standards, USA

E-10 «The Corrosion Behaviour of Ion Implanted AISI 304L and 316L Stainless Steels in Acid and Chlorine-containing Media», C. Ringas and F.P.A. Robinson, Dept. of Metallurgy and Materials Eng., Univ. of Witwatersrand, Johannesburg, South Africa

E-11 «The Corrosion Behaviour of Ion Implanted WC-Ni and WC-Co Alloys in Acid and Chlorine-containing Media», C. Ringas and F.P.A. Robinson, S.B. Luyckx and J.P.F. Sellschop, Univ. of the Witwatersrand, Johannesburg, South Africa

E-12 «Effect of Y, S, Y₂S and Xe Ion Implantation on the Oxidation of Ni», J.M. Hampikian and D.I. Potter, Metallurgy Dept., Univ. of Connecticut, USA

E-13 «The Effect of Ion Implantation, Ion Beam Mixing and its Combined Action on Aqueous Corrosion Resistance», W. Tian, W.P. Cai, J. Li and R. Wu, Wuhan Iron and Steel University, China

E-14 «Oxidation of Nitrogen-implanted Al and Surface Films of Al Oxide», G. Sørensen and H. Jensen, University of Århus, Denmark; S. Lucas and F. Bodart, LARN and ISIS, University of Namur, Belgium

E-15 «Phosphorous Implantation of 304L Stainless Steel», E.C. Cooney, and D.I. Potter, Metallurgy Dept., Univ. of Connecticut, USA; N.L. Lee, General Motors Res. Lab., USA

E-16 «The Effect of Ion Implantation on the Mechanisms of Oxide Adhesion and Hot Corrosion of MCRAIY-type Alloys», V. Provenzano, Naval Research Laboratory, USA

E-17 «Electrochemical Studies of Fe-Cr Amorphous Passive Films Prepared by Ion Beam», X.J. Fan, H.X. Guo, Q.H. Yu, Wuhan University, China

E-18 «Activity and Surface Composition of Sputter Deposited Pt/ γ -Al₂O₃ Catalysts», A. Licciardello, F. Iacona and S. Pignataro, Università di Catania; A. Parmaliana, F. Frusteri and N. Giordano; C.N.R.-T.A.E., Pistunina, Italy

E-19 «Electrochemical and Corrosion Behaviour of ARMCO Fe and a number of Chromium Steels, Implanted with Nitrogen Ions», V.V. Bereza and V.V. Parshutin, Inst. of Applied Physics, Kishinev, USSR; P.L. Bonora and L. Fedrizzi, University of Trento; L. Guzman, IRST, Trento, Italy

E-20 «Oxidation Resistance Studies of Ar⁺ and N₂⁺ Implanted 304 Stainless Steel», D.C. Kothari, L. Guzman, L. Calliari, A. Tomasi and E. Vololini, IRST, Trento, Italy; P. Scardi, Department of Engineering, Trento University, Italy

E-21 «The Effects of N₂⁺ Ion Implantation on the Oxidation of Polycrystalline Cu», D.C. Kothari, L. Guzman, L. Calliari and A. Tomasi, IRST, Povo, Italy; S. Gialanella, Dept. of Engin., Mesiano, Trento, Italy; P.M. Raole, RSIC, IIT, Poway, Bombay, India

E-22 «Electrochemical Study of Multiple Energy Nitrogen Ion Implanted Al Alloys», Y. Massiani and J.P. Crouzier, Université de Provence, France; L. Fedrizzi and P.L. Bonora, University of Trento; M. Elena, IRST, Povo, Trento, Italy

E-23 «The Effects of Ion Implantation upon Ni Oxidation Investigated by SIMS», P.J. George, Kurukshetra University, India; M.J. Bennett, H.E. Bishop and G. Dearaley, Harwell Laboratory, U.K.

E-24 «Relationship Between Properties and Structures under Different Temperatures of Bombardment», T. Wei, L. Jiun, C. Weiping, W. Run, Wuhan Iron and Steel Univ., China

F-6 «Annealing Effects of Oxygen- and Nitrogen-implanted Aluminum», S. Ohira, NIKKEI, Japan; M. Iwaki, RIKEN, Japan

F-7 «Mössbauer Study of the Formation of Metallic Layers by Ion Implantation of Co in Si», A. Vantomme, M.F. Wu, I. Deszi and G. Langouche, University of Leuven, Belgium

F-8 «Structural and Electrical Studies of Vanadium Silicide Layers Synthesized by High Dose Ion Implantation», V.P. Salvi, S.V. Vidwans, A.M. Narsale, A.A. Rangwala, Dept. of Physics, University of Bombay, India; A.K. Jain and Kuldeep, Nuclear Physics Division, BARC, Bombay, India

F-9 «Improvement of Microwave Ion Source for Surface Modification», N. Sakudo, K. Tokiguchi, T. Seki and H. Koike, Hitachi Ltd., Japan; M. Iwaki, RIKEN, Japan

F-10 «Electronic Properties of Al-Mn Quasicrystalline Films Formed by Ion Beam Mixing», X. J. Fan, H. X. Guo, Q. H. Yu, S. Wang and C. Tian, Wuhan University, China

F-11 «The Effects of Nitrogen and Boron Ion Implantation on the Performance of Electric Contacts», S. R. Xu, Y. Zhang, Xi'an Jiaotong University, China

F-12 «Plasma Oxidation of Metals and Semiconductors: Mechanism and Technological Applications», V.A. Labunov, Bielorussian Academy of Sciences; V. P. Parkhutik, Minsk Radioengineering Institute, Minsk, USSR

G-6 «A newly Developed Linear Ion Implanter for Industrial Applications», H. Ranke, St. Reineck, anbd F. J. Körber, Leybold AG, FRG

G-7 «High Current Metal Ion Beams with Energies up to 45 keV/U», H. Emig, D. Rück, P. Spädtke, and B.H. Wolf, GSI, Darmstadt, FRG; B. Torp, Danfysik, Denmark

G-8 «An Investigation on Plasma Assisted Plating System for Thin Film Engineering», Z.B. Hui and W.Y. Ding, SIME, Shanghai, China

G-9 «The Use of Cross-sectional Transmission Electron Microscopy -XTEM- for Depth Selective Microstructural Analysis of Implanted Metals», E. Gernitsen, and H.A.A. Keetels, Philips, Eindhoven, The Netherlands; E. Johnson, H.C. Oersted Institute, Copenhagen, Denmark

G-10 «High Current Density, Broad Beam Ion Implantation», P.J. Wilbur, Wei Ronghua and W.S. Sampath, Colorado State University, USA

G-11 «A New Machine for Combined Physical Vapour Deposition and Ion Implantation of Thin Films», L. Guzman, B. Margesin, V. Zanini and C. Cestari, IRST, Povo, Italy

ABSTRACTS

SESSION A
Fundamentals

A-0

William A. Grant Plenary Lecture

"WILLIAM ALEXANDER GRANT AND THE BEGINNINGS
OF SURFACE MODIFICATION"

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TRANSPORT PROCESSES IN SOLIDS DURING ION IMPLANTATION

by

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ABSTRACT

There are many important effects of fast charged particles irradiation on solid-state rate processes in solids:1)sputtering,2)enhanced diffusion,3)break-up of clusters of precipitated atoms,4)electric fields formation promoted by electronic excitation. In most irradiation studies of solids many different combinations of these effects,depending on the target electronic density,occur together.

In this talk we present a survey on transport phenomena occurring in solids during irradiation, stressing both possible common features as well as peculiarities arising just from the nature of the irradiated solid: metal,semiconductor or insulator.

In particular we will comment on different role of electronic excitations in dielectric solids as opposed to metallic ones.

Basic phenomena occurring during fast charged particles irradiation of solids are described in the framework of transport models.

Particular emphasis will be placed upon recent theoretical and experimental developments concerning correlation processes during atomic migration and ionic transport on percolation clusters.

TEMPERATURE AND DOSE DEPENDENCE OF NITROGEN IMPLANTATION INTO IRON : EXPERIMENTAL RESULTS AND NUMERICAL MODELISATION.

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It has been shown that the depth profile of nitrogen implanted into iron depends strongly with the temperature of the sample during the implantation^(1,2). The nitrogen depth profile shows a surface peak which increases with the implantation temperature. A systematic study of nitrogen implanted iron has been performed with different experimental techniques, and a numerical model has been developed in order to explain this temperature effect :

Pure iron samples have been implanted with 100 keV $^{15}\text{N}_2^+$ (50 keV/atom) to different doses ($2 \cdot 10^{16}$ to $5 \cdot 10^{17}$ N/cm²) and at various implantation temperature (20 °C to 200 °C).

The specimen were studied by Conversion electron Mossbauer Spectroscopy (CEMS) in order to measure the relative concentration of iron nitrides (ϵ -Fe₂N, ϵ -Fe₃N, α' -martensite).

The nitrogen depth profiles were measured with the $^{15}\text{N}(\text{p},\alpha\gamma)^{12}\text{C}$ nuclear resonant reaction ($E_{\text{p}} = 429$ keV)

A numerical model has been developed to explain the shape of the nitrogen depth profile. This model accounts for preferential sputtering, thermal diffusion, radiation enhanced diffusion, secondary phase precipitation and radiolytic decomposition of the precipitates.

The nitrogen surface peak is shown to be the consequence of an enhanced precipitation near the surface. Nitrogen implantation in Copper, Nickel and Molybdenum show that the existence of that peak is correlated with the formation enthalpy of the corresponding nitride.

Ref.

(1) F.Bodart, G.Terwagne, M.Piette, Mater. Science and Engineering 90 (1987), 111

(2) G.Marest, C.Skoutarides, Th.Barnavon, J.Tousset, S.Fayeulle, M.Robelet : Nuclear Instr. and Methods 209/210 (1983) 259-265

SURFACE PRECIPITATIONS OF ION IMPLANTED LITHIUM AND BORON IN METALS

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ABSTRACT

After ion implantation and subsequent annealing of Li and B in metals, frequently surface precipitations are found. Their thermal evolution is analyzed by observation of the surface peaks in the Li and B depth profiles.

In general, surface peaks are found to set in at typically $T = (0.3 \dots 0.4) * T_m$ (T_m = melting temperature), and can be described by trapping of an interstitially moving fraction of the implanted material. This easily mobile component amounts typically to 0,03..30% of the totally implanted ions, the fraction depending on the system under consideration. Observed surface peaks vanish in the case of Lithium by sublimation at typically 500 - 600 C, but remain stable for Boron nearly up to T_m .

In a few cases (e.g. Li in Al and Cu), surface peaks developed at much higher homologous temperatures ($T = \text{ca. } 0.6 * T_m$), which shows that their development is correlated with the substitutional diffusion of Li in the bulk.

In the case of Boron, the surface precipitations of the implanted material are frequently masked by surface precipitations of natural Boron impurities, which are found to be abundant in most metals in the order of typically 1 to 100 ppm atomic.

DISSOLUTION AND REPRECIPITATION OF NITRIDE PRECIPITATES IN CARBON STEEL
BY LOW DOSE α -BOMBARDMENT

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In this contribution we study the effects of post α -bombardment on the dissolution and reprecipitation of carbonitrides present in N_2^+ implanted martensitic low carbon steel ($C = 0.2$ wt%). The characterization of the precipitates is done via Conversion Electron Mössbauer technique (CEMS). In a first step the steel sample is implanted with N_2^+ at an energy of 150 keV and total fluence $\phi = 2 \times 10^{17}$ at/cm², forming $\xi\text{-Fe}_2\text{N}$ precipitates with 60% of the normalized CEMS spectral area. Then, the sample is annealed at 400 °C resulting in the complete transformation of the original $\xi\text{-Fe}_2\text{N}$ into the $\epsilon\text{-Fe}_3\text{(CN)}$ carbonitrate. Subsequent irradiation of the annealed sample with α particles ($E_\alpha = 25$ keV and $\phi = 7 \times 10^{15}$ at/cm²), results in a total dissolution of the carbonitride and reprecipitation of the N, forming a high concentration (50%) of $\epsilon\text{-Fe}_{2+x}\text{(CN)}$. Further annealing of the α -bombarded sample at 450 °C transforms completely the $\epsilon\text{-Fe}_{2+x}\text{(CN)}$ into $\epsilon\text{-Fe}_3\text{(CN)}$. At this temperature still remains a large quantity of precipitates (-22%). Finally, after annealing at 500 °C the CEMS spectrum shows only the characteristic sextet of martensitic steel indicating complete dissolution of the precipitates. We have changed the α implantation fluence between 10^{14} and 7×10^{15} at/cm². For the lowest fluence both precipitates already co-exist, while for increasing α fluence there is a gradual transformation of the $\alpha\text{-Fe}_3\text{(CN)}$ into $\text{Fe}_{2+x}\text{(CN)}$. Finally, we show that the dissolution and reprecipitation are independent of the α particle energy in the range from 25 to 150 keV, but the retention of the precipitates at 450 °C strongly depends on the presence of α particles in the implanted region.

The α -bombardment of a sample containing the original $\xi\text{-Fe}_2\text{N}$ (that is, before the 400 °C annealing which transforms $\xi\text{-Fe}_2\text{N}$ into $\epsilon\text{-Fe}_3\text{(CN)}$) does not produce any effect, but further annealing of this sample up to 450 °C shows a much lower (4%) presence of the $\epsilon\text{-Fe}_3\text{(CN)}$ carbonitrides.

From the above experiments we conclude that the dissolution and reprecipitation of nitrides or carbonitrides by α -bombardment is strongly dependent of the type of precipitate present in the sample. In addition the retention of the precipitates depends on the thermal and irradiation story of the sample.

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COMPOSITION CHANGES WITH BOMBARDED ALLOYS

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The understanding of composition changes with bombarded alloys in 1984 was that the changes correlated badly with mass differences, in sense but not magnitude with binding energy differences, and in sense (but not necessarily magnitude) with surface segregation. A role for segregation was proven only when appropriate composition-depth profiles were found.

The progress since 1984 has included recognizing that segregation-related profiles are normal, that angular distributions give similar information, and that segregation explains not only the sense but also the magnitude of composition changes.

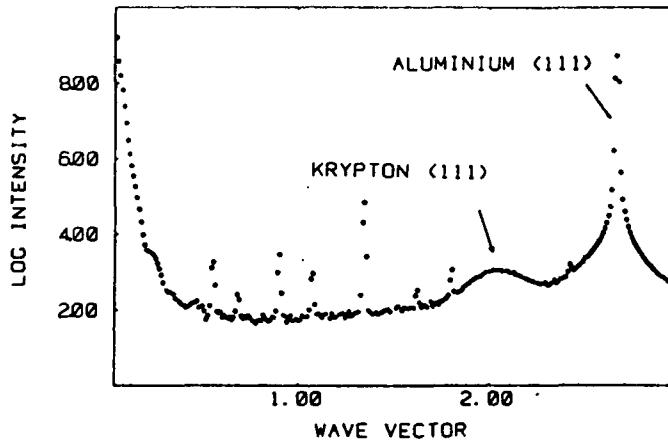
A persistent problem was explaining how the driving force for segregation, typically of order 0.1 eV, could have relevance to a violent particle bombardment. This problem is not unique to segregation, but also arises in attempts to relate atomic mixing with metallic systems to the heats of mixing and to relate composition changes with oxysalts to the heats of formation. The answer to all this work appears to lie in the existence of significant post-cascade atom movement, identified both experimentally and in computer simulation. This movement was, however, specially shown to lead to segregation.

X-RAY STUDIES OF NOBLE GAS INCLUSIONS IN
ALUMINUM SINGLE CRYSTALS.

by

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 Denmark
 and
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Crystalline krypton and xenon inclusions in (111) cut aluminum single crystals were produced by ion implantation at room temperature and analysed by x-ray diffraction. The figure shows an x-ray diffraction scan along the (111) specular direction of the as implanted sample. In addition to the (111)



Bragg peak of the aluminum crystal, there is a distinct although weak (111) peak originating from the crystalline krypton inclusions, which are oriented epitaxially with the aluminum matrix. One of the Kr implanted samples (implanted to a fluence of $2 \cdot 10^{20} \text{ Kr}^+ \text{ m}^{-2}$, at 200 keV) was annealed at 600 K and subsequently cooled to 14 K, the diffraction data revealed that there had been a considerable growth of the crystallites during the annealing, a rough size estimate tells us that the mean size at 14 K was 2.4 nm before and 4.2 nm after the annealing. The data are at present analysed to get a more detailed knowledge of the size distribution of the crystallites. In an aluminum sample implanted with Xe to a fluence of $2 \cdot 10^{20} \text{ Xe}^+ \text{ m}^{-2}$ at an energy of 131 keV we find a mean size of 3.2 nm for the Xe inclusions in the as implanted sample.

We are planning to do a similar analysis on an aluminum single crystal implanted with lead, as this system is also expected to phase separate. Electron microscopy data show that the lead inclusions are faceted and aligned epitaxially with the aluminum matrix (ref. 1).

DYNAMIC MIXING AND ITS APPLICATION IN IMPROVING THE
INTERFACE ADHESION

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ABSTRACT

This paper presents a brief summary of the approaches of improving the adhesive strength between a thin film and a substrate by ion bombardment and experimental results obtained recently. It is found that the adhesion of the thin film deposited on a substrate depends on interface atom mixing and that dynamic recoil mixing is a good method to enhance the adhesion. In order to predict the correlation between the experimental parameters and the thickness of intermixed layer, A Monte Carlo code of dynamic mixing for simulating the process of concurrent ion bombardment during thin film deposition has been developed. The simulation results indicate that the amount of mixing atoms increases with the ion energies. However, a saturation behavior is found at high energies. The ion-to-atom arrival ratio and the mass of projectiles are also the important factors influencing the interfacial mixing. It is expected that an appropriate selection of the experiment parameters, such as ion energy, ion/atom arrival ratio, etc. may be of significance to modify the adhesive property by dynamic recoil mixing.

TITANIUM IMPLANTATIONS INTO A HIGH SPEED STEEL
DISTRIBUTION PARAMETERS AND CEMS CHARACTERIZATION

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The Z85WDV652 high speed steel was implanted with 110 keV titanium ions at 20°C and with fluences varying between 5.10^{16} and 4.10^{17} Ti.cm $^{-2}$. For each fluence, theoretical distributions were calculated taking into account the variation of both the titanium concentration as a function of depth and the distribution parameters (R_p , ΔR_p , skewness, kurtosis, sputtering yield).

A comparison was made between these results and experimental ones. It concerns more precisely the titanium profiling using the ^{48}Ti (p,γ) ^{49}V resonant nuclear reaction at 1362 keV with a GeLi detector and the sputtering yield measurements of titanium and iron.

Moreover carbon and oxygen contaminations were followed as a function of fluence thanks to the RBS technique at high energy. A characterization of the created phases was performed with conversion electron Mössbauer spectroscopy.

NUCLEAR RESONANCE ANALYSIS (NRA) DEPTH
PROFILING OF Na IMPLANTED INTO
ALUMINIUM AND AISI 316 Ti - STEEL^{a)}

by

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ABSTRACT

Na^+ -ions of 250 keV resp. 450 keV energy were implanted at a fluence of $1.5 \times 10^{17} \text{ Na}^+/\text{cm}^2$ into 2 mm thick metallic targets using the 30 μA Na-beam of the Göttingen mass separated heavy ion implanter IONAS. Due to its large atomic radius Na is nearly insoluble in most metals. Therefore the implantation to a maximum concentration of about 9 at% produces a supersaturated solid solution of Na in the targets (polycrystalline Al, Ti-stabilised austenitic reactor steel AISI 316 Ti). To study the thermal behavior of these solid solutions the samples were annealed in a vacuum of 4×10^{-6} mbar for 30 min at temperatures up to 1200 K.

The narrow resonance in the cross section of the $^{23}\text{Na}(\text{p},\gamma)^{24}\text{Mg}$ nuclear reaction at 309 keV proton energy was used to scan the Na depth profiles. The high depth resolution of this technique (typically 50 nm at 200 nm depth in Al) allows the observation of diffusion phenomena at low temperatures. In the case of the Al matrix Na-precipitation in the radiation damaged zone was found followed by Na outdiffusion.

The reactor steel AISI 316 Ti showed a more complex temperature dependence of the observable Na content. For comparison the annealing behavior of implanted Na was also investigated in the individual steel components (Cr, Fe, Ni). The influence of structural TiC precipitates will be discussed.

^{a)}Partially supported by the BMFT under contract 13N 5420/7

CALCULATION OF ION IMPLANT DEPTH PROFILES
AT HIGH DOSE

by

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ABSTRACT

Ion Implantation at high doses, and especially with heavy ions incident on metal targets, produces concentration profiles which are markedly different from those calculated by simple transport codes or even Monte-Carlo codes. These effects are caused by a shifting of the profile due to front surface sputtering as well as a density, and effective atomic number change due to the implanted atoms.

A depth profile modeling program has been written which accounts for many of the important effects present at these extreme dose levels. These include surface sputtering at arbitrary angles of incidence, dynamically changing effects due to composition alteration, parameter changes resulting from compound formation, atomic diffusion, and multilayers of elements, mixtures, and compounds.

The model also includes rotation of cylindrical samples, multiple implant summations, and skewed instantaneous profiles. The basic distribution function is a Pearson I, IV, or VI type as determined using 4 moments. The first two moments (projected range and straggling) are calculated using the latest ZBL (Ziegler, Biersack, Litmark) stopping powers, and the second two moments (skewness and kurtosis) are calculated using empirical fits to experimental profile and Monte Carlo determinations.

Predictions from the code will be compared to published depth profile measurements, and application examples will be given.

SPUTTERING OF COPPER CRYSTALS BY SOLUBLE/NONSOLUBLE
METAL IONS

by

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ABSTRACT

The aim of this investigation is to elucidate the influence of the solubility of the implanted ions on the sputtering process. Copper single crystals were used as target material and bombarded in the <111> direction with 100 keV Sn⁺ ions or 150 keV Pb⁺ ions in a broad range of fluences. Lead is known to be insoluble in copper, whereas tin forms a solid solution with copper at the concentrations attainable under sputtering conditions.

RBS-analysis of the copper crystals show in the case of tin that the surface concentration raises to a saturation value, whereas in the lead case the implantation region is nearly depleted of lead atoms at higher fluences ($>2 \cdot 10^{21} m^{-2}$). However, this strong difference in surface concentration is only partly reflected in the differential sputtering yields of the implanted ions.

Scanning microscopy of the tin bombarded surface shows only a weak topography, whereas in the case of lead bombardments the surface was completely covered with rounded pyramids of predominantly triangular shape.

The non solubility of implanted ions seems mainly to influence the total sputtering yield through the creation of a heavy surface topography. The angular distribution of the sputtered material may indicate that the lead ions induce a structural phase transformation in the surface.

IN-SITU STUDY OF SURFACE DEFORMATION FIELDS
INDUCED BY ION IMPLANTATION

by

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The study of surface deformation during ion implantation gives information about mechanical stresses created in implanted solids which are mainly generated by defects formed by penetrating ions. The aim of paper is to find three dimensional distributions of mechanical stresses in solids as a function of implanted ion type, energy and intensity for materials with different structures.

The wide area surface deformation was experimentally studied by laser-interferometric technique during implantation of He and Ar ions with energies 50-125 keV into silicon and metal wafers. The dynamics of interferometric pictures registered during ion implantation by means of computer technique was translated to surface configuration dynamics in the scale of real time as a function of dose of implanted ions. On the base of received experimental results the model of formation and distribution of mechanical stresses across the implanted samples is proposed. The model includes two surface layers: the top layer where ions stopping energy is distributed and the layer existing beneath it where the long distance compensating mechanical stresses are distributed.

The study of deformations immediately after implantation shows that the redistribution of mechanical stresses is related with the relaxation of implanted layer.

Long distance effects as observation of high densities of dislocations in metals at depths 20-30 μ m from surface and propagating acoustic waves are discussed in connection with the transformations of distribution of mechanical stresses during implantation.

ION INDUCED SURFACE MODIFICATIONS OF COBALT CRYSTALS

by

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ABSTRACT

The channelled sputtering yields of the hcp and fcc phases of cobalt are dependent on the crystal structure and ion induced damage. The aim of this investigation is to explain the influence of the implanted ion species on the sputtering yield in the hcp-phase. Earlier measurements with Ar⁺ have shown that the channelled <0001> sputtering yields are significantly higher than expected in the temperature range 100-3500 C, presumably due to radiation induced damage and ion induced hcp-fcc phase transition.

Sputtering yields have been measured using the weight loss method, on cobalt single crystals bombarded with soluble and nonsoluble ions.

The effect of radiation damage and the occurrence of the hcp-fcc transition are also studied by measuring the angular distribution of the sputtered material and RBS-analysis of the Co-crystals after bombardement.

SESSION B
Ion Induced Phases

TEMPERATURE EFFECTS ON ION IMPLANTED MICROSTRUCTURES

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The temperature of implantation influences several features of ion implanted metals and alloys. In our 1986 SMIB presentations, we examined the way temperature governs three specific features as observed for Ni, Si and Al implantation into nickel and nickel alloys. These features are as follows:

- 1) The surface topography resulting from pit formation and growth.
- 2) The implanted ion concentration vs. depth profiles.
- 3) The phases in the implanted layers and their stabilities.

The temperature affects surface topography by altering the size and density of radiation produced voids. These voids nucleate pits as they emerge via sputtering at the surface. The temperature affects ion concentration vs. depth profiles by influencing radiation induced segregation, recrystallization and subsequent grain boundary diffusion, and volume diffusion. The temperature affects phases and their stabilities in the implanted layers by controlling such processes as ordering of radiation disordered phases, and by causing changes in microscopically localized solute concentration resulting from radiation induced segregation.

Here, within the realm of these temperature dependent effects, we emphasize the role of ion beam flux and energy. Specifically, we examine the stability of precipitate particles and the magnitude of radiation induced segregation to the implanted surface, monitoring the early stages of implantation (fluences $< 10^{16}$ ions/cm²). Thus, Ni ions with energies of 3.0 MeV and others with energies near 180 keV were implanted into Ni-12.7 at.% Si and Ni-12.8 at.% Al. Both alloys contained ordered precipitates. Ion fluxes at 3 MeV were near 10^{12} ions/cm²s, and between 10^{12} and 10^{13} ions/cm²s at 180 keV. Temperatures in each case were investigated from 200°C to 800°C.

Results to date, available only at 3.0 MeV, show precipitate restructuring occurs. Existing precipitates are eliminated and replaced by others, a result of dislocation loops nucleating at particle/matrix interfaces and subsequent radiation induced segregation of elements to these loops. The segregation is slight at temperatures below 300°C, reaches a maximum near 550°C, and diminishes at higher temperatures. The results of similar investigations for lower energy ions, and as a function of flux at these lower energies, will be presented and compared with the 3.0 MeV results.

EXPERIMENTAL AND THEORETICAL DEVELOPMENTS IN ION BEAM
INDUCED AMORPHIZATION

P.M.OSSI #8

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Energetic particle bombardment of thin evaporated films on solid substrates provides a typical case of crystal - glass transition in which the system, which is externally driven, may be far from thermodynamic equilibrium. Changes in the near surface layers through which ions travel are caused both by their very presence, in the case of chemically active species, and by the degree of damage induced during the slowing down processes. Relaxation of collision cascades has dramatic effects, which eventually result in topological, or chemical disordering of the matrix: the extreme case of amorphization depends on the complicated interplay of various factors, such as principally ion characteristics, temperature and target nature. In this work critical experiments, both regarding ion implantation and ion mixing are considered, with the aim to identify important features in this class of glass formation processes. In particular, the currently active research on quasicrystalline materials offers new suggestions about the crystal - glass transition, the relative stability of amorphous phases and their relation to crystalline ones. The existence of chemical short range order in heavily disordered metal glasses constitutes an experimental basis upon which on one side structural models have been constructed and on the other plausible amorphization mechanisms and paths were proposed. Results obtained in the framework of a recent interpretative model of glass nucleation are presented for various types of metallic systems undergoing phase changes under ion bombardment.

SURFACE METALLURGY WITH HIGH ENERGY HEAVY ION BEAMS

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High energy noble gas ion beams are currently used to induce the formation of specific surface alloys from vacuum deposited multilayered thin film structures on metallic or insulating engineering components.

We discuss in this paper the formation of metastable and stable, quasicrystalline and crystalline phases of the Fe-Al thin film bilayer system formed on the surface of insulating substrates by means of high vacuum furnace annealing, ion bombardment of the bilayer interface and the simultaneous combination of these two metallurgical treatments.

PHASE FORMATION DURING ION-BEAM MIXING
OF TRANSITION-METAL MULTILAYERS

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Evaporated films of alternating layers of early and late transition metals have been ion-beam mixed with inert-gas ions for the study of the phase formation during ion irradiation. The mixing was performed with 500-keV Ar⁺ and Xe⁺ which fully penetrate films of thickness ~800 Å. The microstructure was investigated by transmission electron microscopy and x-ray diffraction. The homogeneity and composition were checked by Rutherford-back-scattering spectrometry.

Glass-forming ranges of several binary systems were studied as a function of composition, temperature (30-750K), and ion mass. Besides the amorphous phase, extended terminal solid solutions and, at higher temperatures, some unidentified compounds were observed. The measured glass-forming ranges will be discussed in relation to thermodynamic parameters such as the heat of mixing and equilibrium solid solubilities. Furthermore, the ion-beam mixing amorphization ranges are compared with corresponding ones obtained by other techniques. Finally, amorphization mechanisms in play during ion-beam mixing are discussed.

MIXING AND ANNEALING EFFECTS IN THE Kr-IRRADIATED Fe-Pd SYSTEM

by

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ABSTRACT

Bilayers consisting of 30±35 nm thick layers of Pd on top of a 45 nm thick layer of Fe were sequentially electron-gun evaporated onto oxidized Si substrates. To avoid sputtering effects, a thin layer of C about 5 nm thick was evaporated on top of the samples. Ion mixing was performed at room temperature at doses around $2.5 \times 10^{16} \text{ cm}^{-2}$ of 200 keV Kr⁺⁺. The depth distribution profiles of the different elements in the samples were measured by 1.8 MeV $^4\text{He}^+$ Rutherford backscattering (RBS).

Near the surface RBS shows the presence of a region in which the Fe concentration changes smoothly from about 25 at.% at the surface, to 40 at.% in depth, suggesting the possible formation of well defined Fe-Pd phases which will be identified by X-Ray Diffraction, Conversion Electron Mössbauer Spectroscopy and Transmission Electron Microscopy.

At larger depths there is a region in which the concentration gradients are very steep.

Samples were annealed in the temperature range 300:600°C in forming gas. We observed that the situation reached after irradiation is stable up to a temperature of 400°C, while in the unirradiated samples a diffusion of Fe in Pd takes place even at 300°C. At temperatures higher than 500°C both the unirradiated and ion mixed samples form a surface region with the same equilibrium composition: FePd.

DETAILED ANALYSIS OF THE AMORPHIZATION PROCESS
IN ION-BOMBARDED METALLIC ALLOYS

by

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ABSTRACT

A model of amorphization of crystalline metallic alloys by ion bombardment has been recently proposed [1]. This model is based on the assumption that amorphization occurs via the formation of small amorphous clusters as soon as a given short-range order and a threshold defect concentration are locally reached. All available results are borderline cases where either the chemical short-range order (ion irradiation experiments) or the threshold disorder (ion implantation experiments) are already (or rapidly) established. The purpose of the present work is to check the necessity of the occurrence of these two conditions in the amorphization process.

A partially amorphous Ni-B alloy (with a fraction of amorphous volume $\alpha \approx 0.5$) has been prepared by low temperature B ion implantation, heated above the crystallization temperature and then irradiated with low B ion fluences in order to study the disordering kinetics. The channeling technique was used to monitor the amorphization process.

The results show that a phase separation (mixture of amorphous Ni-B, crystalline Ni and Ni_3B) occurs during annealing. Under subsequent B irradiation, the Ni_3B phase turns amorphous with a kinetics similar to that obtained in pure Ni_3B single crystals [2], while the Ni phase stays crystalline up to B fluences such that the chemical effect due to the presence of B atoms in the irradiated layer becomes important.

- [1] A. Benyagoub and L. Thomé, to be published (1988).
- [2] A. Benyagoub, J.C. Pivin, F. Pons and L. Thomé, Phys. Rev. B 34, 4464 (1986).

AMORPHIZATION PROCESS IN Mn IMPLANTED Al THIN FILMS AND SINGLE CRYSTALS:
EFFECTS OF STRAINS AND TARGET TEMPERATURE

by

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ABSTRACT

The amorphization of Al thin films and single crystals by Mn implantation at LNT and RT was studied by X-ray diffraction, Rutherford backscattering and channeling experiments. Structural changes, the lattice site occupation of the implanted Mn atoms, static displacements of the lattice atoms, the ion implantation induced reduction of grain size, and the accumulation of strain could be directly observed as a function of Manganese concentration. For the LNT implants it was found that at low Mn concentrations (< 5 at%) the impurities occupy mainly substitutional lattice sites ($f_s \approx 90\%$). In this concentration range the atomic size mismatch leads to static displacements of the host lattice atoms. Measurements further suggest that the regions in the immediate vicinity of the Mn impurity atoms are severely distorted. When the local Mn concentration and thus the local distortions exceed a threshold value, the matrix becomes unstable and amorphous clusters are formed throughout the sample. The critical local Mn concentration for amorphization was found to be $c_c = 8.5$ at% and the minimum volume of the amorphous clusters $V_c = 2 \times 10^{-21} \text{ cm}^3$ which is the volume of a sphere with a radius of 3 interatomic distances.

The RT implants showed a drastically reduced solubility, small lattice parameter changes and negligible homogeneous strains. Moreover, a nonzero amorphous fraction is observed at very small Mn concentrations, i.e., no threshold effect is observed in the amorphization curve.

The differences of the amorphization process compared to the LNT case are discussed in terms of thermally activated short-range migration of Mn atoms which leads to the formation of amorphous clusters and to a relaxation of strains at smaller Mn concentrations.

TEMPERATURE DEPENDENCE OF AMORPHIZATION AND PRECIPITATION PROCESSES
IN Ni^+ AND N^+ IMPLANTED $\text{Ni}_x\text{Ti}_{1-x}$ ALLOYS

by

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ABSTRACT

Superficial amorphization and TiN precipitation in N^+ implanted $\text{Ni}_x\text{Ti}_{1-x}$ alloys are known to dramatically improve their tribological properties. This improvement is very dependent on the ion fluence and the implantation temperature. To determine the influence of these parameters on amorphization and precipitation in ion implanted $\text{Ni}_x\text{Ti}_{1-x}$ alloys ($x=0.3, 0.43, 0.5, 0.56, 0.68$) an extensive TEM microstructural characterization of the implanted layer is in progress.

Here, we will present the first results of this study. N^+ and Ni^+ (without chemical interaction with the target) implantations are performed at various temperatures from 77 K to 575 K, and at several fluences, from 10^{13} to 5×10^{15} ions/cm² for Ni^+ and from 10^{14} to 10^{17} ions/cm² for N^+ .

— For 250 keV Ni^+ implantation the full amorphous concentration range is only $0.4 < x < 0.6$ at 77 K, even for the higher fluences, whereas it is $0.25 < x < 0.7$ for room temperature co-sputtered Ni-Ti films.

For $0.25 < x < 0.4$ and $0.6 < x < 0.7$ Ni-Ti crystallites are embedded in the amorphous layer; it is never fully amorphized, even at 77 K and for high fluences such as 5×10^{15} ions/cm², equivalent to an average value of 10 d.p.a.. When the fluence increases the amorphized volume fraction increases to reach a limit which is, at 77 K, approximately, 75% for $0.25 < x < 0.4$ and 35% for $0.6 < x < 0.7$. This limit indicates that, even at 77 K, local reordering, enhanced or even induced by irradiation, competes with ballistic disordering in the cascades. At higher temperatures, an irradiation enhanced homogeneous crystallization process occurs such that, for all the concentrations, the Ni^+ implanted Ni-Ti specimens are crystalline beyond 500 K. This temperature is at least 200 K lower than the thermal crystallisation temperature.

— 160 keV N^+ implantation with a fluence of 10^{17} ions/cm² performed between 77 K and 500 K induces superficial amorphization and TiN precipitation. We show that these precipitates embedded in the amorphous layer are oriented when the amorphisation reaction starts after the formation of the first epitaxial precipitates in the crystalline substrate. This behavior happens at high temperatures, but also at 77 K.

These two results show that, even at low temperature, reordering and interstitial migration which leads to TiN precipitation, can locally occur in the cascades through a low activation energy process (maybe, even athermal) when strong driving forces are present.

TARGET TEMPERATURE DEPENDENCE ON TITANIUM OXIDE FORMATION
BY HIGH-DOSE OXYGEN ION IMPLANTATION INTO TITANIUM SHEETS

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A study has been made of formation process of titanium oxide buried in titanium surface by O^+ -implantation with high doses. Ti sheets were implanted with 150 keV O_2^+ beam density of $1-2 \mu A/cm^2$ with doses of 2×10^{17} to $2 \times 10^{18} O^+/\text{cm}^2$ at the target temperature of -50°C and room temperature during ion implantation. X-ray diffraction patterns of O^+ -implanted Ti sheets were measured to estimate the formation of titanium oxides. In the case of room temperature implantation, X-ray diffraction patterns show TiO formation under the dose of $6 \times 10^{17} O^+/\text{cm}^2$ and show formation of only rutile TiO_2 in exchange of TiO over the dose of $1 \times 10^{18} O^+/\text{cm}^2$. On the other hand, at the target temperature of -50°C , X-ray diffraction patterns show TiO formation even at the dose of $1 \times 10^{18} O^+/\text{cm}^2$, at which the rutile TiO_2 was formed in the case of room temperature implantation. These results show that the structure change from TiO to rutile was not observed in the case of low temperature implantation. This means that the rutile structure formed by ion implantation was induced by not only the oxygen atom injection but also the thermal effect during ion implantation. It is summarized that the structure of titanium oxide was able to be controlled by the target temperature during ion implantation.

T.E.M. STUDY OF AMORPHIZATION AND PRECIPITATION
IN Ni⁺ IMPLANTED ALUMINIUM

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We present here a part of an extensive investigation on ion implantation improvement of aluminium alloys surface properties. This part is devoted to amorphization and precipitation in Ni⁺ implanted aluminium.

For fluences between $8 \cdot 10^{16}$ and $2 \cdot 10^{17}$ Ni⁺cm⁻², low current ion implantation ($I < 2 \mu\text{Acm}^{-2}$) induces a thin amorphous layer which recrystallizes at 200°C, with fine disoriented precipitates. On further heating, a progressive coalescence of the precipitates was observed until a limit size of about 0.22μm was reached at 450°C.

For high current Ni⁺ implantation ($I < 10 \mu\text{Acm}^{-2}$) and the same fluences, a new Al₈₅Ni₁₅ precipitate phase was found in epitaxy with a supersaturated Al₉₅Ni₅ solid solution. These two phases have a f.c.c. structure. There is a slight compression along one of the <001> axis of the precipitate structure. The epitaxial relationships between the precipitates (p) and the solid solution matrix (m) are :

[001]_p // [001]_m
(040)_p // (240)_m

Convergent Beam Electron Diffraction (CBED) analyses show that the solid solution has the 3m symmetry of aluminium. The exact symmetry of the precipitate phase is yet to be determined.

INFLUENCE OF ION BEAM IRRADIATION ON THE SUPERCONDUCTING AND STRUCTURAL PROPERTIES OF THE HIGH-T_C OXIDES THIN FILMS

by

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ABSTRACT

Thin films of the high-T_c superconducting oxides LaSrCuO and YBaCuO, which have been prepared by dc- and rf-magnetron sputtering on single crystalline Al₂O₃, SrTiO₃, ZrO₂ substrates have been irradiated at different temperatures (RT, LN₂, lHe) with various ions. The interest in these experiments concentrated on the sensitivity of T_c to defects, the defect structure, correlation of T_c with resistivity, annealing effects and phase transitions.

The results show that T_c is highly sensitive to irradiation induced defects. The defects appear to be of collisional nature. The effects on T_c and the normal conducting properties are strongly fluence dependent. At low fluences ($<10^{16}$ H⁺/cm²) the resistivity increases without affecting T_c. Medium fluences ($\sim 3 \cdot 10^{16}$ H⁺/cm²) in addition lead to T_c depressions. The shape of the modified transition curves (behaviour of onset, midpoint and zero resistance point), however, depend on the quality (homogeneity) of the films. At high fluences ($\sim 1 \cdot 10^{17}$ H⁺/cm²) a partial transition to a semiconducting phase is observed. X-ray diffraction experiments suggest that defects affecting T_c are mainly due to displacements on the oxygen sublattices. Amorphization is observed by heavy ion irradiation leading to the displacement of equal amounts of atoms on all sublattices as detected by channelling measurements on epitaxially grown single crystalline films.

SOLID RARE GAS BUBBLES IN METALS PROBED BY MÖSSBAUER NUCLEI
by

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Heavy rare gases implanted to a high dose in metals tend to precipitate and form 'bubbles'. Several recent studies deduced the high pressure of these bubbles from measurements of the lattice constant. Some Mössbauer nuclei, like ^{57}Co , have an isomer shift that is rather sensitive to the local pressure and, through their recoilless fraction and quadrupole interaction, are very interesting probes for pressure and pressure induced effects.

We utilized ^{57}Co atoms in Al and Mo, previously implanted with 2.10^{16} Kr atoms per cm^2 , and observed two unique sites: a first one, with a low recoilless fraction and not previously observed, which we could identify as an interface position on the internal walls around the bubbles; the second one was on a substitutional metal lattice position. The latter site was a direct probe of the internal pressure of the metal lattice, which had a clear dependence on the annealing temperature and reached a maximum of about 77 kbar after a 500 K. The pressure at the interface site followed the same trend as a function of the annealing temperature, but with reduced intensity. Measurements inside the solid bubbles, using the ^{83}Kr , ^{125}mTe and ^{133}Xe isotopes, are underway.

SURFACE DEFORMATIONS BY HIGH DOSE MeV ENERGY
He, Ne AND Ar IONS

by

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ABSTRACT

In future thermonuclear reactors MeV energy He ions will hit the first wall of the device, while energetic neutrons will be destroying its crystal lattice. The scope of this paper is to offer a short review on the connected research in our institute.

He ions in the .8 - 3.5 MeV energy range were implanted into various polycrystalline materials as well as single crystal silicon wafers and amorphous metallic glasses. Due to the accumulated He gas the layer above the projected range flaked off or blistered in accordance with the implantation energy and sample temperature. In several experiments the He rich zone of the exfoliated layer as well as the remaining bulk material suffered secondary surface deformations of a similar kind. It was pointed out, that before flaking the induced high lateral stresses caused a regular periodical rippling of the implanted layer in the case of homogenous materials.

Implantations of wide energy distribution showed, that the detaching process initiates at the depth of maximal He concentration.

To model the effect of simultaneous radiation damage, heavier noble gases were also applied. The energy of the Ne and Ar ions were between .3 and 1.4 MeV. In this case the rippling in the implanted layer appeared right on the surface too. The radiation enhanced and stress oriented diffusion led to high cylindrical blisters in the case of 1.4 MeV Ne implanted single crystal Si.

TEM study of the Microstructures of Ion Implanted Steels

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Microstructural changes occurring after N^+ - or Ar^+ -implantation on ferritic and austenitic steels are investigated using the TEM technique. In the case of N^+ implanted ferritic steels, it is observed that the near-surface region gets cracked into polycrystals. The implanted layer has laminar structure with dispersed voids and ϵ - $Fe_{2,3}N$ precipitates. In the case of Ar^+ implanted austenitic steels, many dislocation lines are observed. The qualitative understandings of the above microstructural changes are discussed in this paper.

DIFFERENT CRYSTALLINE STRUCTURES OF RU-RICH METASTABLE
PHASES FORMED BY ION BEAM MIXING OF THE BINARY SYSTEMS
AG-RU AND AU-RU

by

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ABSTRACT

Multilayered samples of binary metal systems were prepared by UHV-deposition of the pure elements onto glass and rocksalt substrates and bombarded subsequently at 77 K by 400 keV Kr⁺-ions. Structural analyses were performed by in situ X-ray diffraction using a Seemann-Bohlin arrangement and by transmission electron microscopy. The investigated systems Ag-Os, Ag-Ru, Au-Os, and Au-Ru have large positive heats of formation (23 to 41 kJ/mol), and therefore in thermal equilibrium the miscibility in the solid state is vanishingly small. For all systems one component has fcc and the other has hcp structure. A first series of investigations was performed using samples prepared on glass substrates. From these experiments the conclusion could be drawn that during ion irradiation an extension of the mutual solid solubilities occurs. As expected the crystalline structures of the terminal phases do not change. In a second series of measurements samples of the four systems were prepared on rocksalt substrates. For the systems Ag-Os and Au-Os we obtained the same results as in the first series. For the systems Ag-Ru and Au-Ru we observed after ion irradiation with high doses two Ru-rich phases, the hcp phase already known before and a new fcc phase.

ION BEAM MIXING OF SELECTED BINARY METAL SYSTEMS
WITH LARGE POSITIVE HEATS OF FORMATION

by

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ABSTRACT

Multilayered samples of the binary systems Cu-W, Ag-W, and Au-W of different overall composition were irradiated at 77 K by 400 keV Kr⁺-ions with doses up to 5×10^{16} ions/cm². In thermal equilibrium these systems have vanishingly small solid solubility of the components corresponding to a large positive value of the heat of formation. The systems Cu-W and Ag-W are known to be immiscible even in the liquid state. Analysis of lattice parameters from our experiments indicate that metastable solid solutions have formed during ion irradiation. This shows that ion beam mixing is a suitable method to produce metastable alloys in systems with large positive heats of formation.

GLANCING ANGLE X-RAY DIFFRACTION AND SEM STUDIES OF
 N_2^+ IMPLANTED TANTALUM.

by

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ABSTRACT

Polycrystalline Tantalum thin foils are implanted with molecular nitrogen ions at an energy of 30 keV and with doses 1×10^{17} ions cm^{-2} and 5×10^{17} ions cm^{-2} , at Room temperature. Different phases formed during implantation are identified using glancing angle x-ray diffraction. Specimen with lower dose (1×10^{17} ions cm^{-2}) shows presence of cubic TaN phase along with hexagonal Ta_5N_6 phase. Specimen with high dose (5×10^{17} ions cm^{-2}) shows formation of hexagonal Ta_2N , cubic $TaN_{0.04}$ phases in addition to cubic TaN and hexagonal Ta_5N_6 . However, no oxy-nitride phases are detected. Presence of phases like Ta_2N and $TaN_{0.04}$ give evidence of N loss taking place during implantation. SEM and resistivity measurements support the above results.

ION BEAM EFFECTS ON Fe-Ni BILAYERS

by

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ABSTRACT

Fe-Ni bilayers obtained by PVD have been irradiated with 100 keV Ar and 200 keV Kr ions in the dose range 5×10^{15} to 5×10^{16} ions/cm² to induce mixing at the interface. Preliminary results by CEMS (Conversion Electron Mössbauer Spectroscopy) show that low dose irradiation in the considered range does not produce detectable structural changes. At the highest dose, however, the structure at the interface becomes that of a highly inhomogeneous Fe-Ni alloy with which small amounts of fcc phase coexist. The occurrence of this structure is discussed in connection with the behavior of magnetic moment and of mean hyperfine field.

SESSION C

Modification of
Mechanical Properties

PHASE TRANSFORMATIONS OF A NITROGEN IMPLANTED
AUSTENITIC STAINLESS STEEL (X10 CrNiTi 189)

by

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ABSTRACT

The available results of research work performed on nitrogen implanted austenitic CrNi steels are contradictory. The following characteristics have been observed:

- the formation of martensite in the austenite, but as well the complete retransformation of martensite into austenite,
- the solution of nitrogen up to high concentrations, but as well precipitation of nitrides at low concentrations,
- an increase, but as well a reduction of the wear resistance.

Therefore, a systematic phase analysis in connection with hardness and corrosion tests is indispensable for the process development.

With austenitic CrNi-steels in the composition 18/9 stress induced transformation into martensite (γ/α') can occur in part. According to the respective surface pre-treatment variable amounts of martensite are encountered in technical components. The two phases feature remarkably different characteristics with respect to the solubility and diffusion of nitrogen and the nucleation conditions of nitrides. However, not only the substrate, but the implantation process and the process parameters, too, can promote contrary tendencies simultaneously. Examples for this feature are:

- dissolved nitrogen stabilizes the austenite, however, introduced as

C-1 (cont.)

projectile, it can start the transformation into martensite via the formation of residual stresses;

- In principle, a high process temperature stabilizes the austenite, but it can as well destabilize it by increased precipitation of chromium nitrides.

The transformation of austenitic CrNi-steels under nitrogen bombardment, therefore, is not in accordance with a fixed pattern, but can go into different directions; so, the phase analysis has to take the following aspects into consideration:

1. the kind and amount of martensite according to the respective surface pre-treatment;
2. the impact of nitrogen on the γ/α' equilibrium;
3. the growth and transformation of nitride phases from γ and α' ;
4. the correlation between nitride formation and $\gamma\text{-}\alpha'$ transformation.

The following process parameters have been used in this study:

surface treatment: electro-polished (γ),
diamond-polished (about 50% α'),
ground (about 85% α'),

temperature range: RT, 200°C, 350°C,

doses: $1-8 \times 10^{17} \text{ cm}^{-2}$,

current densities: $4/40 \mu\text{Acm}^{-2}$.

The analytical methods used are Conversion Electron Mössbauer Spectroscopy (CEMS), x-ray diffraction, and depth profiling by nuclear reaction analysis. CEMS renders it possible to study the magnetic phases (α' , nitrides) and the paramagnetic phases (γ , nitrides) via the analysis of the distribution of the magnetic hyperfine fields respective of the electrical quadrupole splitting. The crystalline phases and textures can be identified by x-ray diffraction. Due to their characteristics shapes, the depth profiles provide information on the diffusion processes in the course of the phase transformation.

The study is of practical and theoretical interest, this is because steels of the category CrNi 18/9, on the one hand, are used frequently, and, on the other hand, provide an insight into the possible developments of steel surfaces by nitrogen implantation due to the coupling of α and γ phases.

MeV N IMPLANTATION IN FE AND Ti: A MICROSTRUCTURE AND HARDNESS STUDY

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Hardness is an important parameter in explaining the complicated processes which take place at a wearing surface. In low energy (100keV) implantation studies however, standard hardness characterizations probe far beyond the implanted layer and thus are influenced by the softer substrate. Furthermore, the lifetime of the nitrogen induced wear resistance enhancement is limited due to the shallowness of the N penetration depth. To overcome these problems micron thick layers are needed, which consequently demands MeV ion implantation.

Recently, we have developed a heavy ion accelerator, dedicated to implantation of high energy (upto 1.5 MeV) ions with high fluences ($10 - 100 \mu\text{A}/\text{cm}^2$). For the first time we will present a detailed investigation on MeV nitrogen ion irradiation of Ti and Fe. In order to modify the N concentration profile, multiple implants with varying energies and doses are applied. Microstructural analysis, using Rutherford Backscattering Spectrometry , X-Ray Diffraction, optical microscopy and Transmission Electron Microscopy will be linked to changes in macroscopic properties, using hardness and abrasive wear studies. As an example, we have subjected a Ti specimen to a dual implant of 1 MeV N^+ , $2.3 \times 10^{18}/\text{cm}^2$ and 150 keV N^+ , $5 \times 10^{17}/\text{cm}^2$. Using RBS it was shown that N was incorporated in the substrate over depths well above the 1 μm range. Also, XRD clearly demonstrated the presence of TiN in the sample. Hardness measurements indicated that the effect of the MeV implantation can be measured with loads upto 200 grams, whereas upon low energy implantation (150 keV) the effect decreases already above 50 grams. This evidences that hardness in MeV modified layers, when compared to keV implanted surfaces, has become a much more reliable quantity.

A FUNDAMENTAL STUDY OF TITANIUM NITRIDE FILMS
DEPOSITED BY ION BEAM MIXING

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Abstract

A study was performed to investigate the influence of process parameters, such as Ti/N ratio, ion energy, temperature and ion bombardment angle on the properties of titanium nitride films deposited on mild steel plates by ion beam mixing.

Deposited films were characterized by scanning electron microscopy(SEM), X-ray diffraction(XRD), X-ray photoelectron spectroscopy(XPS) and through the evaluation of mechanical properties.

Columnar or less distinct columnar structure was observed by SEM. From the results of XRD and XPS, the main constituent was TiN. When Ti/N ratio exceeded 1.5 and the temperature was over 400 °C, Ti_2N and Ti peaks were observed. Microhardness of the films varied widely. High hardness was achieved at $Ti/N \sim 1.0$, ion energy=20~30kV and temperature >200 °C. The adhesion strength was estimated by a scratch tester with acoustic emmision detector. Better adhesion was achieved at higher temperature. The microstructure of the films and the metallurgical structure of the mixing layer will be discussed in detail.

ION IMPLANTATION IN CERAMICS*

by

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ABSTRACT

Ion implantation may increase or decrease the hardness of ceramic materials and generally increases the rupture strength of such materials. The property changes correlate with changes in the microstructure or phase structure. If the sample remains crystalline, the hardness is increased and if it becomes amorphous, the hardness decreases. Both phase structures show higher rupture strengths when tested in four-point bend tests.

The effects of implantation on the rupture strength of sapphire will be illustrated for implant conditions which produce both defect-containing crystalline and amorphous structures. The role of implantation-induced residual stresses on the failure strength will be discussed. Changes in hardness for both sapphire and silicon carbide will be analyzed in terms of the implantation-produced microstructures. The problems of obtaining accurate hardness data for thin surface layers in materials having high hardness-to-elastic modulus ratios will be discussed.

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**ION IMPLANTATION AND FATIGUE CRACK INITIATION:
INTERACTION OF PERSISTENT SLIP BANDS WITH MODIFIED
SURFACE LAYERS**

by

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ABSTRACT

Experiments on nickel have shown that ion beam mixed Ni-Al surface layers have a pronounced effect on the emergence of persistent slip band (PSB) structures during low cycle fatigue, affecting both the numbers of slip bands observed at the surface as well as their topographical morphologies. This is significant because PSBs operating at the free surface are closely associated with processes of fatigue crack initiation in metals. Recent studies indicate, however, that ion beam surface modifications do not necessarily suppress the formation of slip bands in the interior of surface grains, but instead act to inhibit the penetration of PSB's to the free surface. This has been demonstrated by experiments on nickel polycrystals modified by ion beam mixing of vapor deposited nickel-aluminum layers using 0.5 MeV krypton ions at a dose of 1×10^{16} ions/cm². When fatigued to cyclic saturation, these specimens show greatly reduced numbers of surface slip features compared to unmodified nickel. The existence of subsurface PSBs was revealed by etch-restrain experiments in which the 1000 angstrom deep surface modified region was removed by electropolishing. When fatigue loading was reapplied after surface removal, new surface slip offsets were observed in substantial numbers after as little as 1/4 cycle. These slip features have been positively associated with mature PSBs in the bulk grain. Furthermore, these PSBs impinge on the underside of the modified surface layer during fatigue producing large shear strains in the surface layer. The small number of slip bands which are observed in ion beam modified fatigue specimens are believed to result from surface film rupture in response to the localization of cyclic shear strain by subsurface PSBs. It is concluded that effective surface modifications for inhibition of PSB penetration to the surface must produce adherent layers which are able to resist these high local cyclic strains.

Ion beam modification of solid lubricants on metals

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Solid lubricants on metal surfaces can either be sputtered films or burnished powder films. Ion-beam modifications of sputtered MoS_x films has resulted in a considerable improvement of the sliding life of the lubricating film.

The present paper will discuss the structural and geometrical changes of sputtered MoS_x films exposed to inert gas ion beams in the hundred keV range and with doses varying from 10^{15} - 10^{16} ions/cm². The friction coefficient of sputtered MoS_x films in a dry nitrogen atmosphere was measured to be approximately 0.04 both prior and after ion bombardment, but the sliding life increased by a factor of five.

For lubricating purposes MoS_2 is frequently used in powder form, but the adhesion to metal surfaces is then of crucial importance. The present paper will report on two new approaches with the purpose of obtaining low friction metal surfaces. In the first approach molybdenum metal is immersed as anode in a non-aqueous sulphide containing solution. Although in principle similar to anodic oxydation processes, the molybdenum disulfide film formation on the surface is due to an electrophoretic deposition of colloidal MoS_2 particles. Ion bombardment of such films with hundred keV inert gas ions sinters the lubricating film, which has a friction coefficient of ~0.04 in a dry nitrogen atmosphere or equivalent to sputtered films.

As a second novel approach to decrease surface friction of a molybdenum surface 50-100 keV ion beams of sulphur in the milliamperes range has been implanted in molybdenum and characterized by Rutherford Backscattering (RBS) as well as tested with a reciprocal ball tribometer.

EFFECTS OF OXIDE LAYERS ON THE FRICTION AND WEAR OF Ti-IMPLANTED STEEL

by

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ABSTRACT

Ti-implanted 52100 bearing steel was heat-treated in oxygen at temperatures from $T = 300^{\circ}\text{C}$ to 600°C . Friction and wear tests were performed using low speed, high stress sliding contact in air. Auger spectroscopy and SIMS were used to investigate the changes in composition associated with the heat treatment and the tribotesting. A friction coefficient of $f=0.6$ was obtained for all oxidized implanted surfaces; nonimplanted steel also had $f=0.6$ whereas nonoxidized Ti-implanted steel gave $f=0.3$. Wear was confined to the oxide layer, but the behavior changed with oxide thickness. Relatively thin oxide layers (ca. 10 nm) resulted in the formation and transfer of oxide wear debris to the wear track. Thicker oxides (ca 100 nm) wear sheared from the implanted layer on the first pass; Auger analysis of the wear track indicated that failure occurred at the Fe oxide/ Ti oxide interface. Very thick oxides (ca. 1 μm) buckled and cracked, unlike those on oxidized, nonimplanted steel. In addition to causing oxidation, heat treatment caused carbon from the bulk to migrate into the Ti-implanted layer, and at a temperature of 410°C , the Ti-implanted layer was completely carburized. The influence of oxide debris on the friction coefficient was demonstrated by removing oxide films (using ion-milling) from oxidized Ti-implanted substrates.

EFFECT OF ION IMPLANTATION ON FATIGUE, FRETTING AND
FRETTING-CORROSION OF Ti-6Al-4V

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At the SM2IB conference that was held in Kingston, Ontario, in July 1986, we presented some results on the effect of ion implantation on wear of Ti-6Al-4V alloy. This work has now been extended to an examination of the effect of ion implantation on fatigue, fretting and fretting-corrosion of Ti-6Al-4V. Using smooth, rotating-bending type fatigue specimens tested in air at a frequency of 47 Hz it was shown that nitrogen and boron implantation to doses of $2 \cdot 10^{17}$ ions/cm² at 40 keV have no effect on either the S-N curves or the fatigue endurance limit. These results are in marked contrast to the wear tests, which showed that the wear behaviour of Ti-6Al-4V alloy is markedly improved by nitrogen and boron implantation.

Using a Waterhouse type test rig, fretting and fretting-corrosion of crossed cylinders were examined at room temperature in air and sea water respectively. The applied load was 3N, the slip amplitude 30 μ m and the test frequency 50 Hz. Damage was assessed quantitatively by TalySurf measurements and qualitatively by scanning electron microscopy, as a function of the number of fretting cycles. As in the case of linear wear, implantation of boron and nitrogen at 40 keV and to doses of $2 \cdot 10^{17}$ ions/cm², reduces both the coefficient of friction and the fretting wear volume in both air and sea water.

The results obtained, as well as being of practical significance, provide insights into the mechanisms of wear and fretting of Ti-6Al-4V.

* Deceased, 23rd October, 1987.

STRUCTURAL CHARACTERIZATION AND FATIGUE BEHAVIOUR OF A
CARBON - IMPLANTED PURE CRYSTALLINE NICKEL

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ABSTRACT

Pure polycrystalline nickel were implanted with 150 Kev carbon ions to fluences 2×10^{17} ions/cm² at room temperature. Structural characterization of implanted carbon surface layer and its effect on fatigue behaviour were investigated.

The chemical and microstructural changes caused by the direct implantation of carbon into nickel were examined by AES and TEM. It was found that implantation of carbon into nickel results in formation of h.c.p structure nickel, b.c.c metastable structure, Ni₃C compound and amorphous phase corresponding to different carbon concentration layers. The specimens with and without ion implatation were tested in tension-zero fatigue. A 22% increase in endurance limit was found with implantation. The fatigued surface were examined by SEM. The lower rate and intensity of slip bands in implanted materials were found. Grain boundary cracking is also one of crack nucleation mode of modified materials besides slip bond cracking which is the only crack initiation mode of pure nickel. Dislocation arrangement of fatigued surface layer were observed by TEM. There is less dislocation in implanted layer in comparison with high density of dislocations in surface layer of pure nickel.

EXAMINATIONS OF WEAR, HARDNESS AND FRICTION OF N, B, C, AG, Pb, AND Sn
IMPLANTED STEELS WITH DIFFERENT CHROMIUM CONTENTS

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Implantations of nitrogen, boron, carbon, silver, lead and tin in 4 different steels with chromium content of 1.5 - 18 % were performed. The doses applied were 10^{17} - $5 \cdot 10^{17}$ cm $^{-2}$, the ion energy was 50 - 100 keV. 50 keV were applied in a special accelerator designed for tribological applications by FhG. For the higher energy of 100 keV a Varian-Extrion-350 D implanter was used, the samples being mounted in the research and station. Wear and friction of the implanted layers were tested using a pin-on-disc oscillating tribometer. Hardness was investigated using a microhardness tester allowing loads down to 0.05×10^{-2} N. It was found that nitrogen is very effective in hardening steels with high chromium content ($\approx 18\%$), and in decreasing the wear rate in the range of up to 3 orders of magnitude. Microscopic observations of the abraded surfaces show a strong effect of fatigue after tribological stress in the case of unimplanted steels. Implanted surfaces have a smooth abrasive path even after a long period of testing. Boron reduces the wear of hardened X90CrMoV18 in the range of two orders of magnitude. Carbon is very effective in hardening and reducing wear in low chromium tool steel such as 100Cr6 which cannot be hardened by nitrogen implantation. All results strongly depend on testing atmosphere, load, and material of ball in use for friction tests. The implantation of silver, tin, and lead does not change the hardness of the steels investigated. However, a reduction of friction coefficient was found thus reducing also the wear rate.

ION IMPLANTATION IN JAPAN IN NON-SEMICONDUCTOR FIELDS

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In the RIKEN institute, many studies have been made of surface layer modification of various kinds of materials by ion implantation. Materials selected as a first target were iron and iron-based alloys, and surface layers of glassy carbon, diamond, polymers and ceramics have been modified by ion implantation up to now. Implanted species widely ranged from proton to platinum. A wide variety of surface properties of implanted materials has been investigated such as hardness, friction, wear, bending, pulling, corrosion, wettability, optical properties and so on.

In this report, the recent results of implanted metals, ceramics and polymers obtained at my and other laboratories in Japan will be introduced; micro-characteristics of implanted layers are reported with formation of ceramics and buried ceramics in metal surface layers, metallization of surface layers of ceramics, and carbonization of polymers by ion implantation. Macro-properties of implanted materials are also introduced with tribology, wettability, conductivity and so on.

ION IMPLANTATION IN CHINA
IN THE NONSEMICONDUCTOR FIELD

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Since 1978 several institutes in Beijing and Shanghai have been working in the field of ion implantation on non-semiconductor materials. In the last 10 years the field has developed rapidly in China. At present there are 15 units in China, engaged in this field. Three national conferences and one international symposium have been held on this subject. These will be reviewed in this talk.

The applications of ion implantation technology to non-semiconductor industry will be reviewed. Those applications which are economically feasible, according to the author's point of view, will be presented.

The successful experiments carried out in China in the area of application of ion beams to produce superhard materials, biomedical materials and electrical materials will be introduced. Also a brief introduction will be given of the Chinese work in the field of ion beam induced amorphization and quasi-crystalline phase formation.

CHARACTERIZATION OF TRANSFER FILMS ON OXIDIZED TI-IMPLANTED STEEL

by

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ABSTRACT

The friction and wear behavior of Ti-implanted bearing steel (AISI-52100) has been shown to depend critically on the near-surface composition, as determined by the implantation conditions.^{2,3} By changing the fluence of implanted Ti from $0.5 \times 10^{17}/\text{cm}^2$ to $5 \times 10^{17}/\text{cm}^2$, the friction coefficient can be varied from 0.8 to less than 0.3. Friction, in turn, is believed to be controlled by wear debris, which have been found to consist mainly of oxides. In order to investigate the role of oxides, transfer films formed on nonimplanted, Ti-implanted and oxidized substrates have been characterized by transmission electron microscopy and by Auger spectroscopy.

Wear debris contained mainly iron oxides (with some amounts of titanium). Fe_2O_3 was formed in all substrates. Fe_3O_4 also developed in nonimplanted substrates, but not in Ti-implanted substrates. Ti-implanted substrates generated Fe_5TiO_8 debris, but only after hundreds of sliding contact cycles. The morphology of wear debris was highly dependent on the implantation conditions. Very thin flake debris were seen after Ti+C implantation and are associated with low friction coefficients. Compressed "spheres" of debris were formed from nonimplanted substrates and oxidized implanted substrates. Friction coefficients and wear behavior will be discussed in terms of chemistry of debris, adhesion between surface and debris, and the mechanical behavior of superficial layers.

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² I.L. Singer and R.A. Jeffries, "Surface Chemistry and Friction Behavior of Ti-Implanted 52100 Steel," *J. Vac. Sci. Technol. A1* (1983) 317-321.

³ I.L. Singer and R.A. Jeffries "Effects of Implantation Energy and Carbon Concentration on the Friction and Wear of Titanium-Implanted Steel," *Appl. Phys. Lett.* **43** (1983) 925-927.

T.E.M. INVESTIGATION OF STRUCTURAL TRANSFORMATIONS IN Ti, TiAl AFTER N,
C, B IMPLANTATIONS AND FRICTION

by

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ABSTRACT

The structural transformations induced by N or B ion implantation in thin Ti foils were observed *in situ* by T.E.M., using the electron microscope on line with the C.S.N.S.M. implantor. The formed phases and their orientation relationships with the matrix were different from those reported by other authors. In the case of Ti implanted with N ions an epitaxy between planes and directions of dense packing of Ti and Ti_2N , then of TiN and Ti_2N has been found. In other investigations on samples electrolytically thinned from the unimplanted side, Ti_2N did not form, most probably because of an overheating and of C, O contaminations. Similarly, instead of TiB_2 , we detected TiB in Ti implanted with B (in agreement with the phase diagramm). The boride exhibited an orientation relationship with the matrix of the type (111)//(1102). New transformations of the nitrides, borides and also carbides during friction of Ti, TiAl implanted with N, B or C (bulk samples) have also been investigated. Their correlation with the wear resistance of the films will be shortly discussed.

**Friction and wear measurements of oxydized titanium surfaces
bombarded with ion beams in the hundred.keV region**

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Titanium and its alloys have found a number of industrial applications. However, the surface has often to be treated in order to avoid oxydation and excessive wear, and direct nitrogen implantation reduces both oxydation and wear. In the present paper a conventional oscillatory ball tribometer has been computerized, so accurate time dependent friction measurements can be performed. In the wear process of a titanium surface oxydation plays a very important role, so time dependent friction measurements of anodized titanium is a useful approach to tribological studies of this metal. Inert gas ions in the hundred-keV region has been used to modify the anodized film, which appears more smooth after ion bombardment, when studied with SEM. Direct implantation of nitrogen ions in the hundred keV range has been used to initiate nitride formation in the oxydized film and in the underlying substrate. Varying the oxide film thickness and the ion energy, friction coefficients have been measured and the wear tracks have been studied with a profilometer. The perspectives in formation of oxynitride and nitride layers in titanium will be discussed as an alternative to conventional procedures for protection of titanium surfaces such as plasma discharge techniques.

MeV ION BEAM POLISHING OF ANODICALLY GROWN ALUMINA

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In a previous work, we have studied the MeV ion beam enhanced adhesion of gold films on anodically grown alumina (1). One conclusion was that the alumina roughness was an important parameter and it was found that the adhesion threshold as measured using the Scotch tape test could vary by more than four orders of magnitude.

In connection with these results, we present here a study of alumina roughness modification under irradiation at various temperatures and for various impinging ions. Two experimental methods were used : i) an in-situ capacitance measurement as a function of the implanted dose and ii) Rutherford backscattering (RBS) experiments which provide direct evidence of roughness changes induced by implantation prior to the gold film deposition.

We found that the polishing efficiency was increased for heavy impinging ions, i.e. for high nuclear stopping power. The temperature influence was studied in order to check the role of surface diffusion and rearrangement under irradiation.

(1) B. Daudin and P. Martin,
Submitted to Nuclear Instruments and Methods.

DISLOCATION STRUCTURES IN NEAR SURFACE LAYERS OF
PURE METALS FORMED BY ION IMPLANTATION

by

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Experimental results on structure changes in near surface layers of ion implanted polycrystal metals are presented. Implantation of ions of various types has been realized in continuous and frequency pulsed regimes. Ion energy varied within 40 keV to 1.2 MeV. Bulk structural changes which occurred in the depths exceeding the ion range in a target material were studied using the transmission diffraction electron microscopy method. Ion implantation in metals was found to form a developed dislocation structure in a near surface layer which thickness reached $100 \mu m$ and deeper. Besides high density of dislocation loops was observed in a near surface layer of lower thickness. Dependences of a scalar dislocation density and the densities of vacancy and interstitial dislocation loops were plotted vs the distance to the irradiated surface.

Measurements of microhardness and wear resistance performed at various distances from the surface correlate well with electron microscopy measurements. Hence the modified layer thickness in ion implanted targets significantly exceeds the projected ion range.

Three near surface layers with different structures obtained under high dose implantation are considered. Causes of their formation and their role in changing surface mechanical properties are discussed.

THE INFLUENCE OF TEMPERATURE ON THE
PERFORMANCE OF ION IMPLANTED METAL-FORMING
TOOLS

by

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ABSTRACT

It is well known that the temperature during implantation influences the microstructure of ion bombarded steels. In the course of our studies on metal-forming tools we could show a moderate heat treatment subsequent to the implantation to be of great importance, too. The wear of heat treated metal-forming tools was up to 4 times lower than in the as implanted state.

This effect was studied further in a systematic way. The production simulation processes "upsetting between plane parallel dies" and "backward extrusion of cans" were used as model processes for achieving tool wear. Extrusion punches and upsetting dies were implanted with nitrogen, boron and metal-nitrogen combinations. The implantation dose was varied and the tools were heat treated after the implantation in the 200-300 °C temperature region. The tool wear was measured by means of standard techniques during the metal forming process up to a maximum production of 20 000 parts.

The results are discussed in the light of new ideas on the microstructure of implanted steels, and compared with recent relevant Mössbauer studies of similar systems.

EFFECT OF HPIB BOMBARDMENT ON STRUCTURE AND
PROPERTIES OF TN-20 AND VK-8 ALLOYS
by

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ABSTRACT

Taking VK-8 and TN-20 alloys as an example, we show changes in physical and chemical properties and operation characteristics induced by high power ion beams (HPIB) of nanosecond duration. Irradiation was performed using the modified TONUS accelerator which operated in a technological regime with the following beam parameters : $E = 0.2$ to 0.5 MeV, current density of 50 to 250 A/cm^2 , pulse duration of $\tau = 60$ to 100 ns, a beam cross-section of about 200 cm^2 per one pulse and the productivity of 4 to 12 m^2 during an hour. Carbon ions were employed. Electron microscopy, X-ray analysis, secondary ion mass spectrometry, positron annihilation, measurements of microhardness and wear resistance in the process of cutting were employed as investigation methods.

HPIB induced amorphization of metallic bonds, "healing" of microcracks and sharp decrease in grain dimensions during the carbide phase in TN-20 surface, melting and breaks of carbide dimensions in VK-8 alloy. Tungsten and nickel impurity distribution towards the surface and distribution of light ions into a sample bulk were observed. It is interesting to note that a degree of a metallic bond amorphization increases with current density. 2.5 to 3.2 increase in wear resistance in the process of cutting (with respect to control samples) as well as 1.2 to 1.5 increase in microhardness were obtained.

MECHANICAL PROPERTY CHANGES
IN ION IMPLANTED SILICON NITRIDE FOR ROLLING
ELEMENT BEARINGS

by

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ABSTRACT

Ceramic rolling element bearings offer significant advantages over typical steel bearings in numerous applications, including gas turbines. However, to realize these benefits, silicon nitride bearings still require improved damage tolerance, reliability, and reduced contact stresses. Surface modification via ion implantation is therefore being investigated to improve the surface properties of silicon nitride.

Ion Implantation was performed at room temperature using 100keV beams of Nitrogen, Silicon, and Titanium ions for doses ranging from 5×10^{16} to 3×10^{17} ions/cm². Post implantation tests included Knoop microhardness measurements at 5, 10, and 20 gm, 4 point flexure strength, and Vickers fracture toughness. Results show a dramatic sharp "resonance" in near-surface hardness, which increases about 100% at a dose of 1×10^{17} ions/cm² for all three ions implanted. The microhardness increase correlates well with the calculated ion depth. The average flexure strength of the material did not change; however, the strength at very low failure probabilities as represented by the Weibull modulus shows a substantial increase and potential for further improvement.

A finite element stress analysis was also performed which shows the residual stress state induced by the implantation process. The effect this has on the surface mechanical properties and potential bearing performance will be discussed.

INCREASED MICROHARDNESS, WEAR RESISTANCE AND CORROSION RESISTENCE OF
HPIB - IRRADIATED ALLOYS.

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HIGH POWER ION BEAM (HPIB) EFFECT ON METALS AND ALLOYS DURING A PULSE IS
CHARACTERIZED BY FAST ENERGY DEPOSITION IN A NEARSURFACE LAYER WHICH THICK-
NESS IS COMPARABLE TO ION RANGE, BY THERMALIZATION OF THE LAYER TO ABOUT 10^4 K
AND BY FAST BULK COOLING OF THE TARGET.

THE MEASURED THICKNESS OF THE MODIFIED LAYER IS FROM 100 TO 200 WHICH
IS MUCH MORE IN EXCESS THAN AN ACTIV ION RANGE. WE USED 20, 45, R18 AND R6M5
STEELS, SOLID ALLOYS VK-8, VK-6, T15K8, T14K8, TN20, KT16 AND TITANIUM ALLOY VT5
E.T.C.

THE WEAR RESISTENCE OF HPIB IRRADIATED MILLS, CUTTING TOOLS, TAPS MADE
UP OF R6M5 STEEL INCREASED BY A FACTOR OF 2.2 TO 3.5. THEIR MICROHARDNESS
INCREASED BY FACTOR OF 2 TO 3 IN UNQUENCHED SAMPLES AND BY A FACTOR OF 1.3
TO 1.8 IN QUENCHED ONES. THE LARGEST INCREASE AT THE WEAR RESISTANCE IS
OBSERVED IN CUTTING STEEL SHX-15 BY HPIB IRRADIATED TOOLS.

CORROSION TESTS OF TITANIUM ALLOYS SHOWED, THAT INCREASED BY FACTOR OF
1.5 TO 2.2 WITH RESPECT TO NON-IRRADIATED SAMPLES.

MICROHARDNESS, ARTIFICIAL AGEING AND FATIGUE BEHAVIOR
OF NITROGEN-IMPLANTED ALLOY STEEL

by

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ABSTRACT

The main aim of the presented work was to determine the role of low temperature annealing (so called artificial ageing) in microhardness of nitrogen-implanted alloy steel. The steel of composition: 0.40 % C, 0.65 % Mn, 0.25 % Si and 0.95 % Cr was used in experiment.

The relation between microhardness and fatigue properties was also examined.

The samples were 100 keV N_2^+ implanted at room temperature with doses varying from 1×10^{17} at/cm² up to 6×10^{17} at/cm².

Postimplantation annealing at 100, 150 and 200°C was applied to some of the samples. Annealing time was ranged from 3 to 12 hours.

The microhardness of implanted samples was investigated using a Knoop tester. The fatigue properties were determined by means of the vibrating test.

The relationship between microhardness and annealing conditions will be discussed as well as the correlation between microhardness and fatigue resistance.

WEAR RESISTANCE IMPROVEMENT AND STRUCTURAL MODIFICATIONS
OF B⁺ IMPLANTED AUSTENITIC STAINLESS STEEL

by

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ABSTRACT

It is well known that N⁺ implantation improves steel tribological properties ; in general, it is thought that precipitation is responsible for this improvement. Here, a comparative study on ion implantation modification of an austenitic stainless steel tribological properties was performed using boron and nitrogen which can both form hard precipitates with iron.

Mechanically polished specimens were implanted under an ion energy of 160 keV. Wear experiments and friction coefficient measurements were performed using a pin-on-disc machine.

The best wear resistance improvements are found after :

- 10¹⁷ ions cm⁻² fluence for B⁺ implantation, with a decreased wear rate of about 65 %,
- 3.10¹⁷ ions cm⁻² fluence for N⁺ implantation, with a decreased wear rate of about 50 %.

In both cases the initial rapid rise of friction coefficient is significantly attenuated.

For B⁺ implanted specimens and fluences $\leq 10^{17}$ ions cm⁻² TEM observations and glancing X ray scattering show superficial α' martensite formation but no boride precipitation.

From these experiments, which have to be confirmed, it appears that the wear resistance improvement after boron implantation is probably not due to precipitation like for nitrogen implantation but could be due to the superficial martensite formation and/or to boron atoms likely in interstitial sites.

THE EFFECT OF ION BEAM SURFACE MODIFICATIONS ON FATIGUE CRACK INITIATION IN POLYCRYSTALLINE NICKEL

by

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ABSTRACT

The effects of ion beam surface modifications on fatigue crack initiation in fine grain (0.024 mm) and coarse grain (0.290 mm) Nickel-270 were studied. Two ion beam surface modifications were evaluated. One modification consisted of a Ni-75%Al surface produced by evaporating onto the fatigue specimen alternate layers of Ni and Al to a total thickness of 100 nm and ion beam mixing the layers with 3 MeV Ni⁺⁺ to a dose of 1×10^{16} ions/cm². TEM analysis of the surface indicated the formation of an amorphous Ni-75%Al structure. The second modification consisted of self-implantation with 3 MeV Ni⁺⁺ to a dose of 1×10^{16} ions/cm². Surface modified and unmodified specimens were fatigue tested under fully reversed tension/compression at a constant plastic strain amplitude of 2.5×10^{-4} . The evolution of surface fatigue damage was recorded by periodically interrupting the fatigue test and extracting plastic replicas of the specimen gauge section. The Ni-75%Al surface modification significantly suppressed the formation of surface slip band features while the nickel self-implantation produced only moderate slip band suppression. The surface slip band suppression was more pronounced in the fine grain material than in the coarse grain material. Both modifications delayed the initiation of fatigue cracks and extended the number of cycles to failure in the range of 25-35% for the fine and coarse grain nickel. The modifications did not appear to affect fatigue crack growth rates. An understanding of the mechanisms by which the surface modifications suppress the formation of surface slip band features and delay fatigue crack initiation was gained through microhardness studies of the modified surfaces and TEM analysis of the effects of the modified layers on subsurface dislocation structures.

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF
HIGH DOSE NITROGEN IMPLANTED METALS

by

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ABSTRACT

A study has been made of the mechanical properties of high dose nitrogen implanted metals.

The substrates used were polycrystal iron (Fe), chromium (Cr) and titanium (Ti) sheets 1 mm in thickness with a purity of 99.9 %. The ion implantation of N⁺ ions was performed with doses from 7.5×10^{14} to 1×10^{16} N⁺ ions/cm² at an energy of 100 keV. The substrate temperatures during N⁺-implantation were kept -40, 20, 100 and 200°C. The depth profile of atoms in implanted layers was estimated by Auger electron spectroscopy (AES) combined with Ar⁺ sputter etching. The identification of nitrides produced by implantation was investigated by X-ray diffraction (XRD). The near surface hardness was measured by a Knoop hardness tester. The friction coefficients were measured using a Bowden-Leben type friction testing machine.

The results of nitrogen depth profile for the highest nitrogen dose samples showed the rectangular like distribution. The XRD patterns revealed that various oxides were formed in implanted layers. The tendency of change in hardness was different for kinds of substrates, nitrogen doses and implantation temperatures. The change of the friction coefficients was related to the oxides on the surface layers. It is concluded that not only the nitride but also the oxide layers produced by N⁺-implantation play important roles for the modification of mechanical properties for metals.

ANNEALING BEHAVIOUR OF NITROGEN ION IMPLANTED
304 STAINLESS STEEL

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We studied the effect of annealing on the mechanical properties of nitrogen ion implanted 304 stainless steel. We implanted N_2^+ ions at doses of $5 \times 10^{16}/cm^2$ and $10^{17}/cm^2$ into austenitic samples and into samples in which substantial martensite had been produced near the surface as a result of facing on a lathe.

The Knoop microhardness increased as a result of ion implantation in the martensitic samples. The microhardness in austenitic samples remained unaffected. The implanted samples were subjected to isochronal anneals at increasing temperatures in the range 75^0C to 510^0C . In the martensitic samples, annealing produced a steady increase in the microhardness for temperatures upto 420^0C . After annealing at 420^0C the microhardness is 540 kg/mm^2 compared to a pre-implant value of 358 kg/mm^2 . Thereafter, the microhardness did not change appreciably with anneal temperature. This effect is essentially independent of dose in the range studied. Again, austenitic samples remained unaffected.

Grazing incidence x-ray diffraction revealed the formation of nitrides only at the higher dose. The nitrides disappear after the highest temperature anneal.

This evidence points to solid solution strengthening as the dominant mechanism in the present dose range. Dissolved nitrogen is known to harden the martensitic phase and not the austenitic phase. A simple calculation shows that the solid solubility limit would be reached at the lower dose. Thus the higher dose would not produce a higher hardness. The effect of annealing could be to remove implantation induced dislocations. Nitrogen trapped at these dislocations would then become available for solid solution strengthening thereby causing the observed increase in microhardness.

NITROGEN ION IMPLANTATION INTO INTERMETALLIC COMPOUND TiAl

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Abstract

The intermetallic compound TiAl has remarkable high-temperature strength and resistance to oxidation, combined with low density. However, TiAl lacks ductility and is brittle at room temperature. In the present investigation the intermetallic compound TiAl specimens of compositions, 34, 36 and 38 mass %Al, were implanted with 150 keV N₂ ions to modify the surface structures and properties of the specimens. The microhardness and the chemical structures of the implanted specimens were examined by means of microhardness tests, Auger electron microscopy(AES), X-ray photoelectron spectroscopy(XPS) and X-ray diffraction(XRD). It was found that the hardness increased markedly by nitrogen ion implantation, and the ratio of the increase to the initial hardness reached up to 250% for the off-stoichiometric composition, 34% or 38%Al, becoming minimum for the stoichiometric composition, 36%Al. The XPS analysis showed that N1s spectrum involved a peak at a bonding energy corresponding to that of TiN, and that Ti2p or Al1s peak shifted to a half-way position between metal and TiN or AlN. These results indicated that implanted nitrogen atoms are bounded with the metal atoms to form some kinds of their nitrides. The XRD study showed that Ti₂N and AlN were formed in the implanted specimens for the three compositions. It was demonstrated that microcracks, which were revealed by etching the unimplanted surfaces of the specimens, were totally eliminated by nitrogen ion implantation. The remarkable hardening of the implanted surface was considered to result from a solution hardening due to implanted nitrogen atoms and precipitation hardening due to the nitride formation. The disappearance of the stress-corrosion induced microcracks was thought to be associated with the residual compressive stresses and the nitride formation introduced by nitrogen ion implantation.

POST IMPLANTATION HEAT TREATMENT OF NITROGEN
IMPLANTED 440C STAINLESS STEEL

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ABSTRACT

Post-implantation heat treatment was performed on nitrogen implanted 440C stainless steel for varying times and temperatures. The results show surface microhardness changes similar to those found for age hardening alloys. For example, a maximum was found in surface microhardness which was 40% greater than that of the as-implanted, or as-received material. This was achieved in three days of heat treatment at 120°C. Overaging at 120°C occurred in less than six days. Hardness tests as a function of time at higher and lower temperatures did not produce the pronounced effect observed at 120°C.

These surface hardness changes are attributed to second phase formation during the aging heat treatment. Electron Microscopy, Energy Dispersive X-ray Analysis (EDAX) and Auger Electron Spectroscopy (AES) were used in this study to analyze the effect of the nitrogen implantation and the post implantation heat treatment.

TEM and EDAX analyses demonstrated that some nitride phases were formed following implantation and this increased following the aging heat treatment. The two principal nitrides found were CrN and γ Fe₄N. The matrix of the as-received and as-implanted 440C stainless steel was also found to have a BCT martensitic structure (also some Fe-N martensite) with a high dislocation-tangle density.

MECHANICAL PROPERTIES OF CuNi AND FeAl FILMS
PRODUCED BY DYNAMIC ION MIXING

by

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ABSTRACT.

There are many methods to improve surface properties of materials, eg. by use of ion beams, or film coating or both of them simultaneously. For most applications, the crucial problem in all classical coating methods is always the adhesion of the film deposited on the substrate. In this paper, we investigate the influence of a high energy heavy ion beam during the film deposition on the mechanical properties of two coatings : stainless steel substrates with relatively thick films (1.4 μm - 1 μm) of $\text{Cu}_{50}\text{Ni}_{50}$ or $\text{Fe}_{50}\text{Al}_{50}$ alloys using the new technique of ion beam mixing during deposition.

Transmission electron micrographs of the implanted and unimplanted films reveal them to be essentially solid solutions : fcc for CuNi and disordered bcc for FeAl.

Film/substrate adhesion was measured by means of scratch testing under increasing normal load while friction and wear properties were assessed on a standard ball-on-disc tribometer.

For all unimplanted films scratch testing shows adhesive brittle failure right after the start of the scar, under very low normal loads, and during friction and wear testing coating brake-down occurs within one or two turns.

On the contrary, for the implanted films only cohesive failure is observed at critical loads well beyond plastic yielding of both coating and substrate.

The considerable improvement of surface mechanical properties, especially film/substrate adhesion is discussed. Ion beam mixing at the interface during the very beginning of film growth is considered to be of prime importance.

SESSION D
Ion Beam Assisted Deposition

**FUNDAMENTALS OF ION BEAM ASSISTED DEPOSITION: TECHNIQUE
AND FILM PROPERTIES**

by

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This paper reviews work at NRL over the past three years to develop an improved understanding of the ion beam assisted deposition (IBAD) process and to develop a highly reproducible IBAD system for research and applications. As such it does not attempt to review the excellent work in the literature on IBAD films except where there is direct overlap in the materials studied.

The fundamentals treated here include the effects of sputtering, reflection, species distribution, and charge exchange neutralization of the ions, the ion beam enhanced desorption and reaction rates of gaseous impurities on the surface, and the theoretical treatment of the IBAD process by collision cascade or thermal spike models.

System variables discussed include the effects of gas pressure, evaporation rate, ion current, and ion energy on film composition. Important aspects of current integration and ion gun operation are also included for completeness. Data are presented which demonstrate how changes in process parameters effect the film composition and film properties. Most of the discussion centers on silicon nitride and titanium nitride films because these are pathological materials systems for fundamental investigations. Silicon and nitrogen are completely non-reactive in the vapor phase while titanium and nitrogen are highly reactive. Comparison of these two systems allows the separation of physical and chemical effects on film composition (surface vs. bulk chemical reaction).

Finally, unusual structural and mechanical properties of TiN and $Si_{1-x}N_x$ metastable films will be described as well as applications of the films as wear resistant coatings and as optical devices.

SIMULTANEOUS ION IMPLANTATION AND DEPOSITION

by

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The properties of interfaces and coatings formed under simultaneously He^+ and Ar^+ implantation with 30-175 keV were investigated. The following phenomena such as oxygen adsorption on the substrate, distribution of deposited silver atoms in silicon and silicon oxide substrate, composition and physical properties of deposits were studied as a function of ion energy, intensity of implantation and deposition by means of high energy backscattering spectrometry, Auger sputter profiling, X-ray diffraction.

It is shown that all stages of thin film formation are influenced by high energy bombardment. From the experimental results we may conclude that the high energy irradiation during deposition changes interface properties not only as a result of dynamic mixing of atoms but it also sharply changes the adsorption conditions by means of preferential sputtering and ion beam surface activation. The model of activated atoms is proposed explaining experimental results of deposition rate as a function of implantation intensity. If the deposition prevails on the sputtering, the maximum of ion energy loses moves through interface during film growth. On such way the mixed film-substrate layer is formed. It is shown that the distribution of deposited atoms in the substrate induced by high energy dynamic recoil mixing sharply variates if the variation of intensities of deposition and implantation takes place. The phenomenological model of dynamic mixing is proposed. It is shown that the penetration of deposited atoms in the substrate takes place as a result of stochastic mixing of sputtered and deposited atoms in the conditions that deposition and sputtering rate are equal. The penetration process is governed by diffusion laws with diffusion coefficient expressed as a function of deposition and sputtering parameters.

The applications of technique based on the deposition by ion beam sputtering in high vacuum and simultaneous ion implantation to form coatings for industrial modification are discussed.

THE EFFECT OF IONIZATION IN PRODUCING LARGE
INTERMIX LAYERS IN ION PLATING

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An evaluation of three systems (TiN on Fe, Ti on Cu, and Cr on Cu and Fe) have shown gradated or intermixed layers from approximately 100 to 1000 angstroms thick. The principle ion plating process variable related to interface thickness was found to be the relative ionization efficiency which in itself depends on several mutually dependent variables. Experimental programs examined film formation and morphology in both hollow cathode discharge (HCD) and thermionic emission assisted ion plating (TATIP) systems. Film morphology and composition were also examined in addition to the intermix depth.

Data shows that for higher relative ionization efficiencies, zone 2 and zone 3 type structures can be developed at lower bulk temperatures than previously anticipated and that intermixed layers could vary from a sharply defined interface of less than 100 angstroms to broad intermixed layers with evidence of intermix approaching 1,000 angstroms. Auger depth profiling (AES), X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used for examining both morphology and substrate-film interfacial characteristics. The relative ionization was used for comparison purposes and to negate the broad range of problems associated with developing an absolute measure of the percent ionization. An intermix model includes examining back sputtering, thermal diffusion, atomic mixing, ionization enhanced diffusion and ion implantation. An evaluation is made of the various models in relation to the increased relative ionization efficiency and the experimental results.

SURFACE MODIFICATION OF STRUCTURAL MATERIALS
BY
DYNAMIC ION MIXING PROCESS

by

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ABSTRACT

Titanium nitride films were formed on metals and ceramics substrates by a dynamic mixing process. In the process, titanium evaporation and nitrogen ion implantation were done simultaneously. The process of TiN film formation was studied in the following ways.

- (i) Film formation by the dynamic mixing process was hypothetically separated in three stages. 1) N-ion implantation into substrate; 2) mixing of vaporized Ti, sputtered out substrate atoms and implanted N-ions; and 3) steady formation of the TiN film by Ti vapor and N-ions on the surface of the mixing layer.
- (ii) TiN film was formed on the Si substrate and cross-sections of the specimen were observed by TEM (Transmission Electron Microscopy), and electron diffraction. From the TEM images, two intermediate layers were observed between the substrate and the TiN film. The intermediate layers were considered to be the N-ion implanted Si and intermixed layer described in 1) and 2) of (i), respectively.
- (iii) Composition of the intermediate layers was analysed quantitatively by RBS (Rutherford Backscattering Spectrometry), where RBS data was modified by considering the effect of the roughness profile of the TiN coated surface.
- (iv) Field testing of punching tools was done, where TiN (2 μ m thick) was formed on the punch material of WC-Co alloy by the dynamic mixing process. The TiN coated punches showed performance twice as good as that of uncoated punches.

HPIB-INDUCED MELTING AND MIXING IN DEPOSITED STRUCTURES

by

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ABSTRACT

The review of experimental results on ion mixing in single and multilayered structures on surfaces of metals exposed to high power ion beams of nanosecond duration obtained in Tomsk Nuclear Physics Institute are presented.

Au-Cu, Cu-Mo, Fe-Pb, Fe-Pb-Fe, Fe-Cu-Pb, Fe-Cu-Ag, Fe-Ag-Pb systems with 500 to 2000 Å thicknesses of deposited films have been employed. Double films were 4000 Å thick. HPIB irradiation has been performed on TONUS accelerator with technological parameters of a beam in additional chamber. Samples could be synchronously rotated in the chamber. The beam area per one pulse was 100 to 200 cm². The beam composition was 30% H⁺ and 70% C⁺. Ion energy was of E = 0.2 to 0.5 MeV, pulse duration of 60 to 100 ns. The energy density varied from 0.2 to 5 J/cm². Mixing in the layers with amorphous phase formation, metastable states, ordered solutions and new structures (thermodynamically insoluble) which had not been described in the literacy were obtained.

In the given report, continuous ion beam mixing and laser mixing are compared, and advantages of modification under effect of pulsed ion beams are emphasized. One should note good results obtained on silicide formation using pulsed ion beams in the Cornell University Plasma Physics Laboratory.

NEW COMPOUND SYNTHESIS BY ION ASSISTED DEPOSITION (EMPHASIZING
THE HIGH T_c SUPERCONDUCTORS)

by

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ABSTRACT

Energetic particle bombardment of surfaces will change the properties of that surface according to the particle and its energy. This paper is a review of low energy particle bombardment of surfaces during film growth. Both property modifications and compound synthesis are presented. Energetic particle bombardment (100-1000 eV) during deposition alters film properties such as stress, density, electrical resistivity, chemical purity, hydrogen distribution, structure and composition. Changes in microstructure and orientation are found in Nb, AlN and Group IV B nitride films. Synthesis of stable and metastable phases for high T_c superconductors, copper oxides, AlN, and Group IV B mono and higher nitrides are also possible with energetic ion bombardment.

Superconducting $YBa_2Cu_3O_x$ films, with zero resistance at about 87K, have been deposited by dual ion beam sputtering. The ion beam sputtered films (about $1.2\mu m$ thick) are single phase after annealing in oxygen.

In general, the superconducting transition temperature is found to depend on: substrate temperature and ion beam energy, film composition, annealing conditions, and the nature and the magnitude of the substrate/film interaction.

NITROGENATION OF METAL SURFACES BY Ar^+ -ION BOMBARDMENT

by

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ABSTRACT

The ion-induced chemical reactions at metal-gas interfaces have been investigated by XPS and SIMS for nitrogenation reactions. Various metal targets were bombarded with 8-keV Ar^+ ions in nitrogen atmosphere under a pressure of 1×10^{-3} Pa. The formation of nitrides was appreciably promoted by the Ar^+ -ion bombardment of titanium, vanadium, zirconium, niobium and so forth, compared with those by the chemical adsorption. The rate of the ion-promoted reaction in the surface layer was also faster than that of the direct N_2^+ implantation at the same flux as that of the Ar^+ ions.

The kinetic treatments, based on the flux-dependence of the reaction rate, revealed that the saturated ratio of the N/Me (Me :metal) measured by SIMS is related to the reaction rate of the nitrogenation. Among the metals examined, the reaction rate of the nitrogenation of titanium was the fastest, while those of iron, nickel and copper were negligibly slow. It was observed that the rate of the nitrogenation reaction depends not on the mass of the target metal but on the chemical reactivity of the metal with nitrogen, i.e., Gibbs energy of formation of the nitride. The possibility of applying such ion-promoted chemical reactions to surface modifications of materials is also proposed.

STRUCTURE AND PROPERTIES OF TITANIUM CARBIDE GROWN BY
DYNAMICAL ION BEAM MIXING

by

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Titanium carbide coatings have been obtained by ion beam assisted vapor deposition. The experimental apparatus, operating under an ultra high vacuum of 10^{-6} Pa during deposition, consists of an evaporation system with two 8 kw electron guns on line with a 200 kv multi-ions implanter.

The titanium carbide was synthetized at room temperature by simultaneous evaporation of titanium and carbon solids assisted with argon ion bombardment at high energy (120 keV).

Microstructural analyses by Transmission Electron Microscopy (TEM) show that the coatings are homogeneous with very small grains and the diffraction patterns indicate an ordered c.c. crystalline structure of titanium carbide.

Chemical and analytical analyses of these coatings by luminescent glow spectrometry (LGS), secondary ion mass spectrometry (SIMS) and X ray photoelectron spectrometry (XPS) techniques have also been performed.

The tribological behavior of titanium carbide coatings has been investigated by adhesion and wear tests : one μm thick TiC coating, with a specific carbon concentration, shows a very good adherence of the layer on steel and gives a good wear behavior with a low friction coefficient.

MIXING OF METALLIC MULTILAYERS WITH LIGHT IONS

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ABSTRACT

The Grazing X ray Reflectometry technique has revealed to be useful in the investigation of the first steps of the ion beam mixing process. Due to its high sensitivity, mixed layers as thin as a few Å can be detected (1).

Effects of substrate temperature on the mixing rate of metallic multilayers such as NiPt and NiAu with He ions will be reported. In the case of light ions, the cascade regime is linear. So that, at room temperature, the mixing rate was understood quantitatively in the frame of a model assuming the additivity of two fluxes: $J_B + J_{Th}$ where J_B is the ballistic flux and J_{Th} is the flux driven by the gradient of chemical potential (2). A comparison of the mixing rates in the case of light particles (He ions) and heavier ones (Ne ions) γ -radiation will be presented also.

(1) A. Traverse, M.G. Le Boité, L. Névet, B. Pardo and J. Corno Appl. Phys. Lett. 51 (1987) 1901

(2) G. Martin Phys. Rev. B 30 (1984) 1424

PHYSICAL PROPERTIES OF Ti-N THIN FILMS

by

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This paper reports on the preliminary results of the characterization of films of titanium nitride (Ti-N) produced by different techniques. We are interested to evidence the differences of the Ti-N films obtained by reactive sputtering of Ti in a nitrogen-rich ambient (RF sputtering) and by N-implantation during vapor-deposition of Ti thin films (Ion Beam Enhanced Deposition I.B.E.D.)

The overlayers were analyzed by four point probe to evaluate the resistivity and using a Seeman-Bohlin X-ray diffractometer to carry out information about the structure and the stoichiometry of the film. In order to get a complete picture of the chemical and electronic properties of the atoms in this system, the thin films were characterized with several electronic spectroscopies like Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Electron Energy Loss Spectroscopy (EELS). The observed chemical and physical properties of the films strongly depend on both the growth technique and the particular parameters employed.

**FORMATION OF Fe-Ti ALLOYS BY ION BEAM MIXING
IN THE TEMPERATURE RANGE 300 - 600 K**

by

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ABSTRACT

Multilayers of global compositions $Fe_{33}Ti_{66}$ and $Fe_{40}Ti_{60}$ have been evaporated onto NaCl substrates in ultra-high vacuum conditions (10^{-9} T). The ion beam mixing process has been performed with 500 keV Xe^+ ions with a substrate temperature ranging between 300 and 600 K. The induced metastable phases have been characterized by Rutherford backscattering spectrometry of α -particles and transmission electron microscopy. The temperature range for possible amorphization is shown to depend on the overall composition. The amorphization process is preceded at low dose ($\approx 3 \cdot 10^{15} Xe^+ \text{ cm}^{-2}$) by the formation of small FeTi grains ($\phi < 10 \text{ nm}$). At the highest doses ($\geq 10^{16} Xe^+ \text{ cm}^{-2}$) different stationary states are reached depending on composition and irradiation temperature. In this case an attempt is made to interpret these results in the framework of metastable free energy diagrams.

RADIATION ENHANCED DIFFUSION IN ION BOMBARDED
Ag/Ni THIN FILM MULTILAYERS

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ABSTRACT

Radiation enhanced diffusion (RED) was observed during the AES sputter depth profiling of multilayered Ag/Ni thin films. Broadening of the thin (4 nm) Ag layers occurred during sputter profiling and resulted in Ag-Auger-intensity profiles for each of these five layers which were asymmetric, exhibiting a steep leading edge followed by a more slowly decreasing tail. These findings can be interpreted in terms of interface broadening due to two main factors:

1. surface roughening - symmetric broadening.
2. radiation enhanced diffusion of Ag - asymmetric broadening.

With this, it has been possible to separate these factors and to determine the rate of RED.

ION IMPACT INDUCED DIFFUSION: NEW EVIDENCE
FOR A COMPLEX DEFECT MECHANISM

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ABSTRACT

Radiation enhanced diffusion of Ag in a metastable mixed Ni-Ag solid has been observed in real time during AES depth profiling. Bombardment with Ar ions introduces complex defects into the Ag-Ni solid which give rise to diffusion of Ag at room temperature. The rate of diffusion depends linearly on the defect concentration and is proportional to the sputtering rate. We have found that at elevated temperatures (around 100-200 °C) the complex defects tend to dissociate; this leads to a decrease in the diffusion rate in the Ag-Ni system because the dissociation of the complex defects occurs at a rate faster than can be compensated for by the increased mobility of the Ag atoms. In some other material systems an increase in the diffusion rate with temperature has been reported; in these systems the increase in atom mobility seems to be the more relevant factor, determining the temperature dependence. Radiation enhanced diffusion may be one of the major factors contributing to interference broadening in sputter depth profiling; understanding its temperature dependence may result in improved techniques for obtaining better resolved AES and SIMS depth profiles. The complex defect mechanism we describe may be a general mechanism for radiation enhanced diffusion due to ion bombardment.

SESSION E

Modification of Oxidation and of Corrosion Properties

ION BEAM ASSISTED COATINGS
FOR CORROSION PROTECTION STUDIES

by

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ABSTRACT

Ion implantation and ion beam mixing have been used since many years for corrosion protection studies.

They are capable to produce thin layers with well defined composition. Besides stable phases also metastable or amorphous ones outside the limits of the thermodynamic equilibrium with interesting corrosion properties can be obtained. But, with the exception of special cases there is a serious drawback for their practical application, the limitation of layer thickness which is crucial for long time corrosion protection.

Combining ion beam treatment with other vacuum coating techniques like evaporation or sputtering offers the possibility of producing thicker layers without losing the advantages of ion bombardment. In addition also mechanical properties like stress and adhesion can be influenced. Besides metallic coatings also compounds like ceramics with outstanding corrosion and tribological properties can be produced.

In the present review we compare results of corrosion and mechanical tests performed with ion beam assisted coatings like Si, B, Al, Cr, AlN and hard carbon on steels with results of other workers in order to give an impression of the state and potential of this techniques.

**EFFECT OF REACTIVE ELEMENT ION-IMPLANTATION ON
THE HIGH TEMPERATURE OXIDATION OF Ni-25wt%Cr**

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ABSTRACT

The addition of minor amounts of reactive elements, or oxygen active elements such as Y, Ce and Hf, is known to have a number of beneficial effects on the high temperature oxidation of Cr_2O_3 - and Al_2O_3 -forming alloys above 900°C. For Al_2O_3 formers, the scale adherence is greatly improved. For Cr_2O_3 formers, other than the improved scale adhesion, the oxidation rate is also reduced, the Cr_2O_3 growth direction is altered and there is a reduced transient stage resulting in less or no base-metal oxide formation. Many mechanisms have been proposed to explain these reactive element effects. However, the exact reasons for the improvements in oxidation behavior is still in question. The purpose of this study is to further understand these mechanisms by comparing the behavior of reactive elements additions as ion-implanted surface species and as alloying components.

The influence of ion-implanted Y, Zr, Hf and Al on the high temperature oxidation of a Cr_2O_3 forming alloy: Ni-25wt%Cr is studied. Implantation dosages ranged from 1×10^{16} to 1×10^{17} ions/cm². Oxidation behavior of the unimplanted and the implanted specimens were compared after different exposure times under 1 atm. dry oxygen at 1000°C or at 1100°C. Among the reactive elements studied, Al-implantation showed no beneficial effects on the oxidation behavior; implanted areas even showed higher degree of spallation due to effects of radiation damage. Y-, Zr- and Hf-implants all reduced oxidation rates to the same degree. However, while Y- and Hf-implants also improved scale adhesion, Zr-implants did not. Compositions and microstructures across the scales formed on ion-implanted and unimplanted specimens were studied. In particular, the location of implanted species in the oxide scales were followed with oxidation times using secondary ion mass spectroscopy. Comparison of results were made between specimens implanted with different reactive elements and with situations when the elements were present as alloying additions. Possible mechanisms behind the reactive element effects are thus discussed.

SURFACE OXIDATION OF Cu OBSERVED BY
PERTURBED ANGULAR CORRELATION (PAC)
AND RUTHERFORD BACKSCATTERING (RBS)

by

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ABSTRACT

Radioactive ^{111}In is the standard probing atom in perturbed angular correlation measurements (PAC). It is known to trap oxygen atoms with high probability. ^{111}In ions, implanted into a metal or metaloxide subsurface layer are therefore highly sensitive marker to study oxidation phenomena. The microscopic PAC technique probes only the immediate neighbourhood of the marker. In contrast the Rutherford backscattering method (RBS) yields information on the depth distribution of the constituents of the sample. It shows the macroscopic progression of the oxidation front and the overall oxygen concentration. By combining both methods a microscopic picture of the oxidation process may arise in favorable cases.

Some 10^{12} ^{111}In ions were implanted into Cu foils, which were oxidised at a fixed oxygen pressure either isochronally at increasing temperature or isothermally ($T_{ox} = 300-1100$ K). The PAC spectra were taken at room temperature by means of a set-up of $\text{NaI}(\text{Tl})$ or BaF_2 detectors and the hyperfine interaction parameters were determined. These parameters were compared with those obtained in PAC experiments, where ^{111}In has been placed on substitutional metal sites in CuO , Cu_2O and In_2O_3 . Two different oxidation mechanisms seem to be at work: At lower temperature the implanted ^{111}In atoms are essentially immobile and sense the oxidation of the metal matrix. At higher temperatures ^{111}In diffuses and the precipitation of In_2O_3 is favoured.

EFFECT OF CE IMPLANTATION ON THE CORROSION OF ALLOY 800H
IN S-O-C ENVIRONMENT

by

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ABSTRACT

The corrosion behaviour of a wrought austenitic 20Cr-32Ni-Fe alloy (Alloy 800H) in a simulated coal gasification atmosphere at 700°C was studied for exposures ranging from as short as a few minutes to periods of up to 1000 h. The influence of Ce upon the corrosion resistance of the same alloy was established by carrying out identical tests after ion implantation of the specimen surfaces.

The corrosion kinetics were established using discontinuous gravimetric measurements and a range of conventional structural analysis techniques was used to characterise the structures and compositions of the corrosion products formed. Techniques used included optical metallography, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Electron Probe Micro Analysis (EPMA), X-ray Photon Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS) and Secondary Neutral Mass Spectroscopy (SNMS). In addition, early stage nucleation and growth studies were carried out using a hot stage microscope with an environmental chamber attached followed by sequential scanning electron microscopy.

Implantation of 10^{17} Ce ions/cm² was initially found to improve the corrosion resistance but the protective capabilities decreased with increasing exposure time. Possible mechanisms for these observations are discussed.

ELECTROCATALYTIC PROPERTIES OF ION IMPLANTED
OXIDE FILMS

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ABSTRACT

Implantation of high energy ions causes a radiation damage (formation of Frenkel defects) as well as a doping by the ion stopping in the oxide layer. This modifies the electrocatalytic activity and makes such systems interesting for energy conversion, fuel cells and electrocatalysis /1/.

In continuation of recent experiments /2/ we implanted oxide films with metal ions, e.g. Pd and Ru. The noble gas Xe has non-catalytic activity. Therefore Xe implanted oxide films yield a separation of the radiation damage from chemical effects by doping. While the radiation changes the electronic properties of the whole passive film the concentration of surface states (metal atoms or ions) dominates the electrocatalytic behaviour. These properties of the implanted oxide films were tested by measuring the electron transfer reaction (ETR) of different redox systems in a potentiodynamic scan. Outer sphere reactions (e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$) are suitable to test the electronic conductivity of the film, inner sphere reactions (e.g. H_2 -oxidation, O_2 -reduction, Cl_2 -evolution) are used for tests of surface properties.

A special effect was seen by repassivation of a Pd implanted TiO_2 electrode: During the potentiodynamic scan up to 5 V the Pd-ions become mobile and move to the surface. The Pd enriched layer shows an enhanced activity.

The activation energy of the electron transport was measured by variation of the temperature. The results of these experiments were compared with other techniques of modifications.

/1/ G.K.Wolf, Nucl. Instr. Meth. 182/183 (81) 875

/2/ J.W.Schultze, L.Elfenthal, K.Leitner, O.Meyer, Electrochim. Acta,
in press

LOCALIZED CORROSION BEHAVIOR OF ALUMINUM SURFACE ALLOYS
PRODUCED BY ION BEAM MIXING AND ION IMPLANTATION

by

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The corrosion behavior of aluminum surface alloys produced by ion implantation and ion beam mixing and the mechanisms involved in passive film breakdown are discussed in this paper. Anion adsorption, the first step in pit initiation, is described by a model based on surface charge considerations and the pH of zero charge of an oxide, pH_{pzc}. For example, in neutral solutions, the surface of a high pH_{pzc} oxide such as aluminum, consists of acidic (positive) sites, which are receptors for Lewis bases like Cl⁻, whereas the surface of a low pH_{pzc} oxide such as molybdenum, is composed of basic (negative) sites, which inhibit Cl⁻adsorption. This model predicts that the surface charge of an oxide such as aluminum oxide can be changed by introducing other oxide-forming elements into the oxide film and thereby increasing or decreasing the pitting potential. Experimentally, to date, all of the ion implanted elements selected because of the low pH_{pzc} of their oxides (Si, Cr, Zr, Nb, and Mo) have produced binary surface alloys that had higher (more noble) pitting potentials than aluminum, and the implant chosen because of the high pH_{pzc} of its oxide (Zn) produced a binary surface alloy that had a lower (more active) pitting potential than aluminum. Ion implantation, also, provides a means to change the mechanical properties of the oxide and has provided information on events occurring at the oxide/metal interface. Ion beam mixing techniques have been used to produce Mo-Al surface alloys with higher surface concentrations of Mo and that have a greater pitting resistance than pure aluminum or the ion implanted Mo-Al surface alloys.

Improved High Temperature Oxidation Behaviour of Alloys by Ion Implantation

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Numerous studies have been undertaken during the last decade or so examining the potential of ion implantation to improve the high temperature oxidation of a range of metals and alloys. Most of these have focussed on improved mechanistic understanding of the role of particular elements. Ion-implantation studies have provided unique information, in particular, concerning the effect of the so called reactive elements. In view of this success it is now pertinent to consider whether the process might be utilised industrially to provide improved high temperature corrosion protection to high integrity alloy components for high technology applications. The current status of such a development involving the 20Cr/25Ni/Nb stainless steel fuel cladding for the UK advanced gas-cooled nuclear power plants will be described.

CORROSION STUDIES OF REFRACTORY
METALS IN HOT ACIDS BY ION BEAM
TECHNIQUES

by

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ABSTRACT

Titanium corroding in hot oxidizing acids as HNO_3 stays in the passive state, however, the corrosion rates are rather high.

Since Ti is a preferred construction material for chemical industry appropriate means for corrosion protection are of great interest. Materials with lower corrosion rates in acids are Zr, Nb and Ta. However, alloying of these elements with Ti without degradation of the bulk properties is restricted by the phase diagram. Therefore, we tried to produce surface alloys of Ti with higher concentration of the alloying element by ion implantation and ion beam mixing.

Ta was implanted into titanium with different doses and its corrosion behaviour studied in comparison with the pure metals and conventional 3% or 10% Ti/Ta-alloys. Similar experiments were performed with Ti/Nb-, Ti/Zr- and Ti/Ta-surface alloys obtained by ion beam mixing. The corrosion tests applied were current/potential measurements, and determination of dissolution rates by neutron activation analysis and polarography.

It turned out that the Ti/Ta-system was the most promising choice. The highest implantation doses resulted in reduced corrosion compared to the conventional alloys. The Ti/Ta-alloy obtained by ion beam mixing was even better and had a very good long term corrosion behaviour.

Electrochemical and Corrosion Behaviour of BN Coated Aluminum Alloys Surfaces

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Reactive Ion Beam Enhanced Deposition (RIBED) has proved to be a very effective surface treatment in order to obtain thick, homogeneous and protective coating. In a previous work we showed the very promising role of RIBED obtained boron and chromium nitride coatings in order to reduce the corrosion rate of ARMCO iron. In this work, which is part of a wider study concerning the aluminum surface treatments, we present some results concerning the corrosion behaviour of industrial aluminum alloys coated with a thick BN layer obtained by RIBED.

The BN film was produced by 11 sequential steps, each consisting of a 26 nm B deposition, followed by a N_2^+ implantation to a total dose of $15.8 \times 10^{17} N^+/cm^2$.

For sake of comparison, BN layers 3000 Å thick were also obtained on pure aluminum and on aluminum alloys by the magnetron cathodic sputtering technique.

All the treated samples were then tested in different aqueous environments. The corrosion rate was measured in sodium hydroxide and sodium sulphate solutions at different pH values (3.2, 10, 12), whereas the pitting corrosion susceptibility was evaluated in sodium chloride solutions.

Electrochemical techniques were used to obtain cathodic and anodic polarization curves, galvanic corrosion data and the corrosion rate as a function of time.

Before and after the corrosion tests, the morphological and chemical characterization was performed by using Scanning Electron Microscopy and electron spectroscopy techniques.

The results are discussed in terms of the chemical reactivity, defectivity and structure of the produced BN coatings.

THE CORROSION BEHAVIOUR OF ION IMPLANTED AISI 304L AND 316L
STAINLESS STEELS IN ACID AND CHLORIDE-CONTAINING MEDIA

by

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ABSTRACT

In the present investigation, the pitting and general corrosion behaviour of AISI 304L and 316L stainless steels ion-implanted with chromium and molybdenum was studied. Ion implantation was carried out at various fluences over the range 1×10^{15} to 1×10^{27} ion/cm². The composition of the passive films after implantation was studied by Auger electron spectroscopy.

Although implantation was found to decrease the corrosion rate by as much as 50%, it tended to decrease the pitting resistance. The decreased pitting resistance may be attributed to the formation of an inhomogeneous passive film.

THE CORROSION BEHAVIOUR OF ION IMPLANTED WC-Ni AND WC-CO ALLOYS
IN ACID AND CHLORIDE-CONTAINING MEDIA

by

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ABSTRACT

Alloys of WC-Co (6-30% Co) and WC-Ni (6-15% Ni) were implanted with nitrogen, chromium and molybdenum ions. The corrosion resistance was assessed by accelerated electrochemical techniques, such as potentiodynamic and pitting scans in acid and chloride-containing media. Molybdenum implantation was found to have a beneficial effect on the corrosion resistance of the alloys. This was due to an increase in the passive range and a substantial raising of the pitting potential (E_p)

EFFECT OF Y, S, Y+S AND Xe ION IMPLANTATION
ON THE OXIDATION OF Ni

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The oxidation rates of nickel were determined following implantation with Y^+ , S^+ , Y^+ and S^+ , and Xe^+ ions. Fluences of 3×10^{17} ions/cm² were implanted into the surfaces to be oxidized, and the resulting composition profiles were found by Rutherford backscattering spectrometry. The samples were then oxidized in air at 1 atmosphere in a thermogravimetric microbalance. The oxidation temperature range investigated was 700-1100°C.

The role of implanted ion diffusion on oxide scale formation and morphology was investigated by comparison with unoxidized specimens annealed in ultra high vacuum at equivalent temperatures. Annealing in vacuum at temperatures above 500°C and below 1200°C revealed that yttrium migrates toward the surface, an effect opposite that expected from normal diffusion. The resulting surface microstructures, investigated by TEM and EDX, contained Ni-Y intermetallic phases, confirming these results. Yttrium's role in improving oxidation resistance of structural alloys has been linked to its chemical combination with and immobilization of elements such as sulfur.¹ This suggestion will be tested here, as it applies to nickel, by comparing specimens implanted with both Y^+ and S^+ to specimens containing these elements implanted individually.

¹ J. G. Smeggil, A. W. Funkenbusch and N. S. Burnstein: Metall. Trans., 1986, vol. 17A, pp. 923-932.

The Effect of Ion Implantation, Ion Beam Mixing and its Combined Action on Aqueous Corrosion Resistance

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Abstract

A study has been made to compare the effect of ion implantation, ion beam mixing and its combined action on the subsurface of iron. Pure iron with and without Ti^+ ion implantation, Ti^+ -deposited Fe which then undergo Ar^+ ion beam mixing or was bombarded with N^+ or O^+ ion beam, the last one is called as combined effect of ion implantation and ion beam mixing. By comparing the aqueous corrosion resistance on surface modified by above different treatment. The best results can be got in the case of combined effect. There is a good evidence that the incorporating ion implantation with ion beam mixing has much better effect than that of individually treatment, the critical current density I_c and minimum anodic passive current density I_m are decreased by one or two orders of magnitude. TEM has been performed to characterize the structure. During N^+ or C^+ ion bombarded here, recoil implantation and cascade mixing take place, that is to say, Ti film atoms and Fe substrate atoms are mixed in the Ti/Fe interface region; because of the light ion implanted, there is a thin amorphous alloy formed in the outer layer of the sample.

OXIDATION OF NITROGEN-IMPLANTED ALUMINIUM AND SURFACE FILMS OF ALUMINIUM OXIDE.

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A well known surface-modification process of aluminium is anodic oxidation (1). Further, in recent years, there has been a considerable interest in synthesizing aluminium nitrides by direct implantation in order to modify the tribological properties (2).

Since in the wear process of aluminium, oxidation effects play an important rôle, it has been the scope of the present study to investigate oxidation effects of nitrogen-implanted aluminium and aluminium oxide/aluminium systems.

Pure aluminium and anodized aluminium have been bombarded with $^{15}\text{N}_2^+$ beams in the energy range of 100-500 Kev. The surface roughness was measured with a Dektak profilometer, and the surface stoichiometry was investigated by Rutherford Backscattering Spectrometry (RBS), Nuclear Resonant Reaction Analysis (NRA), and X-Ray Photoelectron Spectroscopy (XPS).

Following the nitrogen implantation, the implanted surfaces were oxidized in order to increase the thickness of the oxide film. The surface composition, and roughness was then remeasured.

The results indicated that the stability of ion-synthesized nitrides and oxinitrides of aluminium largely depend on the field gradient in the anodic oxidation process. These finding are correlated with friction measurements in dry and wet nitrogen atmospheres in a oscillatory tribometer.

- (1) G.Amsel, J.P. David, C.Ortega, S.Rigo and J.Siejka. *Nucl. Inst. Meth.* **149**, 705 (1978).
- (2) S. Ohira, M. Iwaki. *Nucl. Inst. Meth.* **B19/20**, 162, (1987).

PHOSPHORUS IMPLANTATION
OF 304L STAINLESS STEEL

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Electropolished 304L stainless steel specimens were implanted with phosphorus ions to fluences from $0.2 \times 10^{17} \text{ P}^+/\text{cm}^2$ to $6.0 \times 10^{17} \text{ P}^+/\text{cm}^2$. The ion energy was 175 kev, the implant temperature less than 50 degrees centigrade, and the implantations were performed at pressures near 3×10^{-3} torr. Microstructural characterization of the samples with an analytical electron microscope revealed an FCC to BCC phase transformation at low fluence ($0.6 \times 10^{17} \text{ P}^+/\text{cm}^2$) followed by amorphous phase formation which peaked at $4.5 \times 10^{17} \text{ P}^+/\text{cm}^2$. This is followed by a second BCC transformation from the amorphous phase at $6.0 \times 10^{17} \text{ P}^+/\text{cm}^2$.

Composition versus depth profiles were measured using both Auger spectroscopy and Rutherford backscattering spectrometry. Maximum phosphorus concentrations occurred at depths of 500 to 1000 angstroms, with phosphorus concentrations of 30 atomic percent in the amorphous phase. Anodic polarization experiments, performed on specimens with the amorphous phase, indicated a hundred fold decrease in the critical anodic current density, as compared to unimplanted 304L stainless steel. The current required for passivation was also reduced significantly.

THE EFFECT OF ION-IMPLANTATION ON THE MECHANISMS OF
OXIDE ADHESION AND HOT CORROSION OF MCrAlY-TYPE ALLOYS

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Ion-implantation has been used as a tool to investigate the role of oxygen active element additions on the oxide scale development and the low temperature hot corrosion (LTHC) behavior of MCrAlY-type coatings. To this end, cast CoCrAl specimens were ion-implanted with either yttrium, hafnium or cobalt. Following the ion-implantation, both oxidation and low temperature hot corrosion studies have been conducted on the partially ion-implanted specimens. The oxidized and the hot corroded specimens were subsequently examined by scanning and transmission electron microscopies, by energy-dispersive X-ray analysis and by Rutherford backscattering spectroscopy. It has been observed that voids formed on the alloy at the metal/oxide interface during the oxidation process. The size and the density of these interfacial voids were dependent on the oxidation temperature and the exposure time. The formation and growth of these interfacial voids is known to significantly reduce the adhesion of the protective oxide scale to the metal surface during exposures of the alloy at elevated temperatures in aggressive environments. Ion-implanted yttrium or hafnium greatly suppressed the growth of the voids on the coating alloy, whereas implanted cobalt had little effect on void growth. It is believed that the formation of the voids on the unimplanted surfaces is the result of a Kirkendahl-type of effect. As for the hot corrosion exposures, the LTHC attack was markedly more severe in the yttrium-implanted surfaces than in the unimplanted or the cobalt-implanted or hafnium-implanted surfaces. Moreover, little difference was observed in the LTHC response between the unimplanted alloy and the alloy that had been ion-implanted with either cobalt or hafnium. For all experimental conditions, the degree of LTHC attack on the alloy surfaces increased with exposure time. Mechanisms will be proposed to explain both the enhanced LTHC attack observed in the yttrium-implanted cast CoCrAl and the suppression of void growth during oxidation observed in the alloy previously implanted with either yttrium or hafnium.

ELECTROCHEMICAL STUDIES OF Fe-Cr
AMORPHOUS PASSIVES FILMS PREPARED BY ION BEAM

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ABSTRACT

Amorphous Fe-Cr surface alloy passive films have been formed on the steel both by Ar ion beam mixing and by B, P ion implantation in order to improve localized corrosion resistance. The resulting surface alloys were chemically characterized by Auger electron spectroscopy. The corrosion behaviour of these specimens was evaluated by means of the multi-sweep cyclic voltammetry in the electrolytic solutions. TEM observation indicates the presence of the amorphous phase. The results show that both ion mixing and ion implantation can produce the stable amorphous surface alloy passive films on the steel, without the interface of the film-substrate.

In this paper, we report our experimental results of improving the corrosion resistance of some steel work-pieces.

ACTIVITY AND SURFACE COMPOSITION OF SPUTTER DEPOSITED Pt/ γ -Al₂O₃

CATALYSTS

by

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Simple and dual ion beam sputter deposition techniques have been used for preparation of Pt/ γ -Al₂O₃ hydrogenation catalysts. These have been characterized by using surface tools like ESCA (XPS). The activity of the surfaces has been measured and compared with that of an impregnated catalyst. These activities have been related with surface composition. The direct bombardment of the growing film in the dual ion beam deposition is shown to appreciably affect the catalytic activity of the platinum-alumina system.

ELECTROCHEMICAL AND CORROSION BEHAVIOUR OF ARMCO IRON
AND A NUMBER OF CHROMIUM STEELS, IMPLANTED WITH
NITROGEN IONS

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Samples of ARMCO iron and of steel with varying content of chromium (1-25%), nickel (2 - 13%), molybdenum (3%) and titanium (1%) were investigated after nitrogen ion implantation.

Structure modifications (by means of SEM analysis) as well as electrochemical and corrosion behaviour were analysed. Some assumptions are introduced concerning the nature of the surface alloys being formed. New chemical phases were evidenced by means of X-ray diffraction analysis. The chemical composition of the alloys seems to affect the final distribution of nitrogen.

An improvement of both corrosion resistance and strength characteristics of a number of samples was shown up. An actual increase of corrosion resistance of the surface layers is considered to be the consequence of inter grain boundary absence. The influence of carbon, that enters the alloy compositions, on the corrosion properties of the alloys is observed. Thus, the interaction of passivating elements with carbon leads to the formation of inert carbide inclusions, that suppress passivation and initiate local corrosion.

The phenomenon of prevailing dispersion of some of the alloy components and formation of layers with modified composition, connected with diffusion processes in the region adjacent to the surface, was observed. An increase of diffusion under the radiation influence within the boundaries of the modified layers (and perhaps even deeper) was noted.

Electrochemical polarization measurements , in a monomolar solution of sulphuric acid , allowed to determine activation-passivation transition of the materials under investigation, while pitting corrosion resistance was studied in a buffer solution of sodium chloride with a pH = 5

OXIDATION RESISTANCE STUDIES
OF
Ar⁺ AND N₂⁺ IMPLANTED 304 STAINLESS STEEL

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Preliminary studies of nitrogen and argon implanted 304 SS indicate that the nitrogen implantation deteriorates the oxidation resistance whereas the argon implantation makes the surface more oxidation resistant. This behavior can be understood as a cause of possible depletion of Cr due to the nitride formation in the first case and because of Ar induced amorphization of the surface in the second case. To verify these preliminary experiments and the possible suggested mechanisms a systematic study is presently undertaken. The implantations are carried out at 160 keV at various doses. The specimens are characterised by thermogravimetry, low angle XRD, SEM, and AES. The experimental results will be presented and the possible mechanisms will be discussed in detail.

EFFECTS OF N⁺ ION IMPLANTATION
ON THE OXIDATION OF POLYCRYSTALLINE Cu

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The effects of introduction of nitrogen in Cu on its oxidation behaviour are not studied extensively, probably because of insolubility of nitrogen in Cu. Ion implantation is a promising technique to introduce nitrogen athermally into Cu. The oxidation behaviour of nitrogen implanted Cu was studied by Naguib et al¹. They observed the increase in oxidation rate for low dose specimens and the decrease for high dose specimens. To understand this behaviour completely, the present study is undertaken. The N⁺ implantations are carried out at 30 keV. Thermogravimetric measurements are taken at various temperatures. The characterization of specimens before and after oxidation is done by AES, SEM and XPS. Low temperature oxidation results are found to be similar to those of Naguib et al¹. High temperature oxidation studies show lower oxidation rate in initial stages of oxidation, for high dose specimens. In the later stages the oxidation rate is similar for all the specimens. This correlates well with the observed decomposition of nitride formed, above 250 C, reported in the literature. The decrease in oxidation rate seems to correlate well with the presence of nitrogen chemically bonded to Cu.

1. Naguib et al , J Vac Sci Technol, 13 (1976) 396

Electrochemical Study of Multiple Energy Nitrogen Ion Implanted Aluminum Alloys

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Nitrogen implanted aluminum is reported to show a better pitting corrosion resistance. The corrosion behaviour appears to depend on the number of nitrogen atoms available at the surface and the thickness of the implanted layer.

In single energy implantations the number of N atoms available at the surface is lower than that in the bulk, because of the Gaussian nature of the depth profile obtained. To overcome this difficulty, we decided to obtain a thick implanted layer and a flat depth profile by using multiple energy implantations.

Aluminum specimens were bombarded with N⁺ ions in three implantation steps of 80, 35, and 15 KeV energy to a total dose of 4.6×10^{17} N⁺/cm² to obtain a 2000 Å thick homogeneous layer of implanted surface.

The implanted specimens were tested for corrosion resistance in Na₂SO₄ solutions at different pH values ranging from acidic to basic conditions. Cathodic and anodic polarization curves, galvanic corrosion data, corrosion potential vs time plots were obtained for implanted and unimplanted specimens.

The samples were also characterized by SEM and AES before and after the corrosion test.

THE EFFECTS OF ION IMPLANTATION UPON
NICKEL OXIDATION INVESTIGATED
BY SIMS

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and

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ABSTRACT

The influence of the ion-implantation of several elements has been studied upon the thermal oxidation of polycrystalline, high purity, nickel, in oxygen, at 500-1100 °C. The oxide thicknesses and the location of the implanted elements within the scales were determined by SIMS depth profiling. The study concentrated on the effect of yttrium implantation, with the derivation of the dependences upon ion dose, time and temperature. The possible role of the associated physical damage introduced by ion-implantation was examined by comparison of the Y⁺ results with those for krypton implantation and also following post-implantation vacuum annealing. The effectiveness relative to yttrium implantation of the implantation of other reactive elements, cerium, lanthanum and ytterbium, as well as silicon, either alone or in combination with yttrium, was also established.

Relationship Between Properties and Structures under
Different Temperatures of Bombardment

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Abstract

The combined effect of ion implantation and ion beam mixing of iron surfaces is discussed. Pure iron samples deposited with Ti films of different thickness, bombarded with N^+ ions under different temperatures have been studied. Conclusions have been obtained as follows

1. The corrosion resistance of the samples subject to ion combined effect is improved significantly, and is much better than that of Fe or Ti-deposited Fe with and without Ar^+ ion beam mixing.
2. The temperature of bombardment plays an important part in surface modification. A thin TiN amorphous alloy is formed under RT bombardment, so that the corrosion resistance is improved remarkably, the critical current density I_c and anodic passive current density I_m decrease more than one order of magnitude. With a rise of temperature, the surface structures changed, the amorphous alloy on surface disappears.
3. The thicker the Ti film is, the higher the corrosion resistance get, but the thickness of Ti films is not so important to corrosion resistance as temperature of implantation. As soon as passive film formed, the corrosion resistance is increased immediately.

SESSION F

Thin Film Metallurgy for Microelectronics

THE CURRENT STATUS OF METALLISATION IN INTEGRATED CIRCUIT APPLICATIONS

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With the progression towards increased packing density in integrated circuits, more and more emphasis has to be given to solving metallisation problems. Interconnection resistance, high current density, and design complexity are forcing process engineers to use metals other than the traditional aluminium alloys and to use multiple levels of interconnection. Metallisation processes can now represent more than 50% of the fabrication process. Enhanced deposition techniques are being utilised in an effort to reduce contact resistance and to give reliable metallisation over high aspect ratio features where planarisation of both interlayer dielectric and metal layer is becoming essential in the most complex metallisation schemes. In this paper the current status of integrated circuit interconnection and metallisation will be reviewed. The requirements of metallisation in devices will be described from both the electrical and fabrication points of view. Particular emphasis will be given to the use of ion beam techniques e.g. ion beam cleaning, reactive ion beam etching, dual sputtering of alloys, bias sputtering and back sputtering for conformal deposition and planarisation. The use of dynamic recoil mixing for the preparation of low resistance contacts and novel alloy layers will be described. Where appropriate, results from the author's laboratory will be presented.

METALLIZATIONS USED IN INTEGRATED CIRCUITS
AND
ION BEAM EFFECTS

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The properties of a metal film can be changed by using an ion beam either during or after the film deposition. Ion beam assisted deposition and ion mixing are examples of the use of ions for changing the properties of the metallization. Ion sputtering with preferential erosion is also another aspect of ion/metal interactions. After reviewing the results obtained with ion mixing with emphasis to compound formation and metastable phases, will be presented the possibilities offered by the ion beam assisted deposition technique. With this technique it is possible to produce films with unique properties in terms of composition, mechanical properties and structure. Sputtering is also another aspect of ion/matter interaction. We will present the most recent result of preferential sputtering of alloys as a function of the kind of ions and their energy.

A METAL VAPOR PLASMA SYSTEM FOR THIN FILM METALLURGY

by

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ABSTRACT

A metal vapor plasma system that can generate metal, predominantly singly ionized plasmas from a wide range of metals is being used to generate thin films for microelectronics and other applications. The system is presently being used for research into developing techniques for filling high aspect ratio holes in microelectrical devices, generating Fresnel zone plates for x-ray microscopy and applying very thin (0.3) highly reflective coatings for heat shielding. In addition, very smooth, thick coatings of metals such as Cu, Al, Ni, and Pu can be put down at high rates. RMS values of 300 Å are common for thicknesses of 200 microns. It is possible to bias the substrate while coating. The system is unique for the following reasons.

- (1) It has a magnetically confined plasma which is ionized using microwave energy via electron cyclotron resonance heating.
- (2) A very high ion to neutral ratio exists, 100/1. ($n = 10^{12}/cm^3$ at background pressures of 10^{-6} Torr are common.)
- (3) Mostly singly ionized plasmas are generated, 90%.
- (4) Large areas up to 15 cm in diameter can be treated in the present machine.
- (5) Pure metal plasmas can be generated with many metals.
- (6) High deposition rates (greater than 1 μ /min can be obtained from most metals.

The design of the MVP machine is discussed along with some results on our metal fill-up experiments for High Aspect Features in Microelectronics.

PROPERTIES OF OXIDE AND NITRIDE LAYERS IN ALUMINUM
PRODUCED BY HIGH DOSE ION IMPLANTATION

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ABSTRACT

The crystalline and electrical properties of oxide and nitride layers in aluminum produced by high dose implantation of oxygen and nitrogen ions were investigated. High dose of oxygen (4×10^{18} ions/cm²) and nitrogen (2×10^{18} ions/cm²) molecule ions were implanted into polycrystalline and single crystal aluminum sheets using low current densities of 150 keV at room temperature. The implanted layers were characterized by means of AES, XPS, X-ray diffraction, transmission electron diffraction and microscopy. The electrical resistivity and breakdown electric field strength of oxide and nitride layers were measured by current-voltage characteristics.

It was shown that high dose oxygen ion implantation produces microcrystalline γ -Al₂O₃, whereas implanted nitrogen leads to polycrystalline or single crystal AlN layers without any thermal annealing, and it is possible to form insulating layers in aluminum using ion implantation techniques.

Furthermore, the difference of the phase formation between oxide and nitride by high dose implantation into aluminum was discussed. The conduction properties of insulating layers were also described.

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Ar ION BEAM EFFECT UPON PHOTOEMISSIVE THIN FILMS

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This work is concerned with photoemissive materials such as Na_3Sb and $Na_2K Sb$ deposited on glass substrates under UHV conditions. Auger Electron Spectroscopy (A.E.S) associated with optical transmittance and reflectance measurements have been performed during thin film growth and ion bombardment.

Let us first consider the growth of the thin layers. The A.E.S. and optical measurements are used to determine surface composition and bulk optical complex index ($\hat{n} = n-ik$) of the material versus growth time (or thickness). The goal is to achieve thin films which are homogeneous in a direction perpendicular to its surface. This feature is assumed to be obtained when the surface composition as well as the optical constants (n and k) as deduced from A.E.S and optical analyses respectively remain constant with respect to the film growth time.

The second step is concerned with Ar ion bombardement effect on such films. When applied to those films, it induces optical changes of the material. It is demonstrated that the film goes from homogeneous to heterogeneous composition in depth. Auger analyses also show a large surface composition evolution in terms of alkali to antimony ratio.

As an example, the surface of an initial Na_3Sb material is successively made into $NaSb$ and then almost pure Sb in the course of the ion bombardment time. So, the surface composition goes from the material exhibiting the greatest alkali content (smallest binding energy between Na and Sb atoms) to the poorest one. The chemical binding energy between atoms appears to control the bombardment-induced composition changes at the surface and in depth as well.

The physical perturbation takes place in the films up to 1000 Å in depth. As a result, ion milling technique applied on such materials for A.E.S. profiling analyses cannot be related to the actual composition of the film existing before ion bombardment.

Finally, ion beam effects upon materials can be really well analysed with the help of a surface analysis technique (A.E.S) associated to optical reflection and/or transmission measurements.

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ANNEALING EFFECTS OF OXYGEN- AND NITROGEN-IMPLANTED ALUMINUM

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ABSTRACT

We have shown that high dose oxygen and nitrogen molecule ion implantation into aluminum can result in the formation of microcrystalline Al_2O_3 and crystalline AlN layers at room temperature without any thermal annealing.

In this study, the effects of post-implantation thermal annealing on the concentration profiles of implanted ions and the formed structures were investigated. The thermal annealing treatment was carried out at 300°C for 1 hour in a vacuum ambient. The distribution of implanted oxygen and nitrogen before and after annealing was measured by means of AES combined with argon sputtering. The change of crystalline structure after annealing was examined by X-ray diffraction. The difference in behaviour between oxygen and nitrogen in aluminum was observed by AES depth profiles of oxygen- and nitrogen-implanted annealed specimens, whereas annealing did not produce any structural transformation.

From these results, the process of compound formation by high dose oxygen and nitrogen implantation into aluminum was considered, and the mechanism of self ion-beam induced crystallization, which we introduced for explaining an ion beam synthesis of crystalline compounds, was also discussed.

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MÖSSBAUER STUDY OF THE FORMATION OF METALLIC LAYERS BY ION
IMPLANTATION OF Co IN Si

by

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Buried silicide layers were formed by implantation of Co in Si at different energies (up to a dose of 2×10^{17} atoms/cm²) at a target temperature of 280°C. The ion beam consisted of ⁵⁹Co, which was alternated with a small fraction of ⁵⁷Co, the radioactive parent of the ⁵⁷Fe Mössbauer isotope. After implantation, this system was thermally annealed at temperatures up to 1200°C. After annealing above 800°C, the Mössbauer spectrum of CoSi₂ appeared. Rutherford Backscattering Spectroscopy measurements were performed simultaneously, and show the formation of a buried Co-silicide layer.

The buried CoSi₂-layers show an anomalous Mössbauer spectrum. Although this silicide is known to be cubic (and therefore is expected to give rise to a single line Mössbauer resonance) the spectrum always contains a rather broad side resonance, with an amplitude depending on the annealing temperature. This side resonance indicates that a large fraction - typically 20 to 30% - of the Co-atoms has a non-cubic surrounding. Possible origins of this phenomenon are considered.

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STRUCTURAL AND ELECTRICAL STUDIES OF VANADIUM SILICIDE LAYERS
SYNTHESISED BY HIGH DOSE ION IMPLANTATION.

by

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ABSTRACT

It has been reported earlier that high dose ion implantation of $(^{51}\text{V})^+$ ions into silicon produces coherent silicide layers [1]. This technique has many potential advantages over the conventional techniques of forming silicide layers. 30 KeV ions are implanted to the doses ranging from 1×10^{20} i/m^2 , to 5×10^{21} i/m^2 , into single crystal silicon and a-Si films, thermally deposited on SiO_2 substrates. The evolution of silicide phases in the layers have been studied as a function of isochronal anneal treatment, using XRD and RBS techniques. The as implanted layers are mixture of all vanadium silicide phases, which tend to convert to a silicon rich phase VSi_2 . The sheet resistance and resistivity show a gradual decrease due to the decrease of defects produced by ion implantation on annealing and also due to the changes in the silicide phases. The resistivity value saturates to the value close to that reported for VSi_2 phase. Barrier height measurements using schottky diode structures will also be reported in this paper.

[1] V.P. Salvi, et al, Surface Sci., 189/190 (1987) 1143.

IMPROVEMENT OF MICROWAVE ION SOURCE FOR SURFACE MODIFICATION

by

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ABSTRACT

Ion beam modifications of metal surface layers to new metastable alloys require various kinds of ion species. Microwave ion sources have been used to produce high current metallic ion beams[1], [2]. Most metallic elements as source materials can be obtained in the form of solid or liquid halides, which are more easily vaporized than solid metals. However, the usage of halides requires mass separation of ion beams, which limits implant currents.

To increase mass-separated implant currents, the ion beam characteristics should be matched to the mass-separator optics. For this purpose, the beam qualities of the ion sources need to be studied. Thus, the authors have developed an apparatus that can measure the profiles and emittances of beams and can experimentally evaluate the degree of matching between an ion source and the mass-separator optics. It consists mainly of an emittance measuring device, a mass separator and a beam profile monitor. The entire system is controlled by a personal computer, which also processes the data obtained. This apparatus can handle high-power beams of up to 2 kW. In addition, the ion-optical parameters of the mass separator can be varied by remotely changing the entrance and exit angles of the ion beams.

Slit-shaped beams from a microwave ion source were measured with the apparatus. It was found that the mass-separator transmission was mainly limited by emittance deterioration corresponding to the length of the ion source slit rather than the width. The emittance for the length depends on the plasma density distribution along the slit, which was found to be closely related to the vapor-inlet system of the plasma chamber. With this determination of what limits the transmission, the conditions for further improving the implant currents of metallic ion species were obtained.

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ELECTRONIC PROPERTIES OF Al-Mn
QUASICRYSTALLINE FILMS FORMED BY ION BEAM MIXING

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ABSTRACT

Alternating Al-Mn layers are deposited on quartz and Al₂O₃ substrates which are placed on a variable temperature target of 200 KeV implanter. The multilayered films are irradiated with Ar ions. Mixing at 100-200°C produces the icosahedral phase for concentration of Mn between 10 and 20 at% while mixing at 77 K produces an amorphous phase.

"In situ" annealing at successively higher temperatures produces the transformation sequence: amorphous \rightarrow icosahedral \rightarrow crystalline. "In situ" electrical resistivity variations measured continuously both during the ion bombardment and during the annealing show these phase transformations. A model is proposed to explain the observed kinetics.

THE EFFECTS OF NITROGEN AND BORON ION
IMPLANTATION ON THE PERFORMANCE OF
ELECTRIC CONTACTS *

by

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ABSTRACT

The article studies the effects of ion implantation on the performance of electric contacts. N^+ and B^+ was implanted to some kinds of electric contacts, then a make and break test and other tests were made with the electric test machines. Parameters of weight loss of contacts, temperature rise, contact resistance and transfer of material between ion implanted contacts and unimplanted contacts were measured and some valuable results have been got. With the contacts implanted by ion, especially by Boron ion, all of the parameters after the make and break tests were decreased as compared with those unimplanted. It has been shown that it is very promising to improve electric contacts by ion implantation.

* The project supported by National Natural Science Foundation of China

PLASMA OXIDATION OF METALS AND SEMICONDUCTORS:
MECHANISM AND TECHNOLOGICAL APPLICATIONS

by

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ABSTRACT

The process of metal and semiconductor oxidation in low-temperature oxygen plasma is studied both experimentally and theoretically.

Experimental work has comprised a design of multi-task generator of oxygen plasma, study of kinetics of oxidation of metals (aluminium, tantalum, zirconium) and semiconductors, as well as analysis of chemical composition of oxides by XPS, AES and EDX facilities. The kinetics of oxide growth obeys linear law in a plasma of glow hot-cathode discharge with several stages of different growth rates. Chemical composition of plasma oxides resembles that of stoichiometric oxides obtained by thermal oxidation, although the former exhibit a transition region at oxide/substrate interface of disturbed stoichiometry and segregated oxide phases.

Theoretical research has tackled problems of increasing oxide growth rate, clarifying the role played by various plasma particles in oxidation process as well as simulation of electrophysical properties of oxide films.

Present state of the art and future prospects for technological applications of plasma oxides are reviewed.

SESSION G

**Equipment and Industrial
Applications**

ION BEAM PROCESSING FOR INDUSTRIAL APPLICATIONS

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Ion beam processing, well established in the semiconductor industry, is steadily evolving in a wide diversity of other applications. Its acceptance depends on technical merit, economic considerations, competing processes and highly individual hurdles or barriers to acceptance for each particular application.

This talk will discuss some of the most promising applications of ion beam processing in the framework of the considerations mentioned above. Application areas to be discussed include tooling, medical products, and aerospace components such as precision bearings. Examples of recent surface modification developments involving ion implantation, ion beam mixing and ion assisted deposition will be discussed and compared from an industrial perspective.

IMPROVEMENT IN FRICTION
AND WEAR OF HARD CHROMIUM LAYERS
BY ION IMPLANTATION

by

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ABSTRACT

Hard chromium layers are widely used for coating of fiber-guiding elements in the man-made fiber industry. A low wear rate and a time-independent, constant friction coefficient (not necessarily minimized) are essential to this application. A screening implantation program with single or multiple implants has been carried out on hard chromium layers which had galvanically been deposited on steel cylinders. Experimental procedure, equipment, and post-implantation analysis methods are described. The evaluation of friction and wear shows a clear improvement after most ion beam treatments. Its relative degree is dependent on the wear conditions and the ion species. For the wear couple of TiO_2 -pigmented polyester yarn against chromium under abrasive/corrosive conditions, very high gain factors in wear (up to 52) are found. It is also demonstrated that a desired combination between time-dependent change of friction coefficient and specific wear rate can be adjusted by proper selection of the ion beam process.

ION IMPLANTATION IN WC-Co : ANALYSIS OF TREATED SURFACES AND
TESTING OF INDUSTRIAL TOOLS *

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Conventional microhardness and indentation (scratch) testing has been conducted on cemented tungsten carbide samples implanted with nitrogen ions at 90 keV as a function of ion dose and sample temperature during implantation. The main results obtained are:

- (i) N-implantation can increase the surface hardness up to 40 %;
- (ii) the optimum dose lies between 1 and 3 E 17 atoms/cm² for the different grades evaluated and an excess dose can cause softening;
- (iii) there is little variation with implantation temperature of the hardening effect between 140 C and 400 C, no hardening is observed at 550 C, with a reduced hardness increase obtained at 70 C.

A programme of industrial trials, considering several different applications of WC-Co tools, has been commenced. In particular, field tests of drills and routers were conducted by a company specialising in computer-controlled drilling and cutting out of glass fiber/epoxy printed circuit boards. Preliminary results will be reported, together with microanalysis of the treated surfaces.

(*) The following industrial partners are involved in the research: C.S.T. Circuiti Stampati, Trento; GKN BOUND BROOK Italia, Brunico; ACCIAIERIA DI BOLZANO; PIRELLI Cord Metallico, Pigline Valdarno; SANDVIK Hard Materials, Coventry, U.K.; TECVAC, Cambridge, U.K.

**A UNIVERSAL HIGH CURRENT IMPLANTER
FOR SURFACE MODIFICATION OF MATERIALS**

by

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ABSTRACT

A new high current implanter dedicated for surface modification of materials has been developed and is now in operation at the Danish Tribology Centre* in Aarhus, Denmark. The implanter contains a high current multipole-reflex-discharge ion source, "CHORDIS", and produces mass analysed beam currents in the 5 - 10 mA range at energies up to 200 keV. A versatile ion beam focussing system combined with a two dimensional magnetic beam scanning offers high flexibility in shaping of the implantation area (up to 40 x 40 cm²) and control of local current densities. The large target chamber contains a remote controlled water cooled sample manipulator with one linear and two rotational movements. Continuous sample and temperature monitoring and interlock prevents overheating of surfaces during implantation.

The paper describes the general design of the implanter as well as ion beam performance and operational experience from implantations of "industrial" samples.

* (a collaboration between Jutland Technological Institute, Institute of Physics, Aarhus University, and Danfysik A/S)

PLASMA SOURCE ION IMPLANTATION,
A NEW APPROACH TO ION BEAM MODIFICATION OF MATERIALS
by
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Surface modification by ion bombardment is a well established technique for improving the hardness, friction, wear resistance and corrosion resistance of materials. Surface modification of materials by conventional ion implantation is a line-of-sight process in which a directed beam of energetic ions is rastered across a target. If the target is three dimensional, the process generally requires target manipulation to achieve implantation of all sides of the object. This target manipulation requirement can seriously limit the cost effectiveness of ion implantation relative to more conventional surface treatments, especially for large and/or heavy targets. We are developing a new technique, Plasma Source Ion Implantation (PSII), which circumvents the line-of-sight restriction of conventional ion implantation. In PSII, targets to be implanted are placed directly in a plasma source chamber and are then pulse-biased to high negative voltage (10-100 kilovolts in our experiments). A thick, ion matrix sheath² forms around the target, and ions accelerate through the sheath drop and bombard the target from all sides simultaneously without the necessity of target manipulation. Although the PSII process bears superficial resemblance to existing techniques such as "ion plating", "ion coating", or "plasma nitriding", PSII produces a deposition profile characteristic of high energy ion implantation. Our experiments have demonstrated that PSII: (1) efficiently implants ions to the concentrations and depths required for surface modification, (2) produces material with improved microhardness and wear properties, and (3) dramatically improves the life of manufacturing tools in actual industrial applications. For example, in recent industrial field tests the tool life of M-2 pierce punches used to produce holes in mild steel plate has been increased by a factor of 70-80. This talk will present the latest results from a series of ongoing field tests, recent extensions of the technique to ion beam mixing and ion beam enhanced deposition modes of operation, and a discussion of the comparative economics of surface modification by PSII relative to conventional ion implantation.

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A newly developed linear ion implanter
for industrial applications

by

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ABSTRACT

In the paper presented the special design of an ion implanter for industrial use is described. The ion source is a special development and is based on high frequency electrodeless plasma generation. With a slit formed three electrode systems a line shaped ion beam with a transverse length of 30 cm can be extracted and accelerated. Because of the special design of the ion source and power coupling the gas pressure in the source can be prominently reduced which proves to be advantageous with regard to the residual gas pressure in the process chamber. Because of the linear arrangement of the extraction system, the ion implanter is designed for continuous processing large area surfaces, such as foils, metal plates or a larger number smaller parts. Actually the maximum ion beam current amounts to 20 mA at 150 kV. In the scope of the presentation, first results will be discussed.

HIGH CURRENT METAL ION BEAMS WITH ENERGIES UP TO 45 KEV/U

by

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ABSTRACT

The high current ion source CHORDIS⁺ is intended to generate dc and pulsed beams of at least any element with mA-intensities. Beside gas and oven versions of this ion source, a sputter version has been developed and investigated with titanium, copper, molybdenum, and tantalum electrodes. Stable beams of these metals can be extracted from the source for several hours.

The CHORDIS source is used at GSI at a 50 kV test bench and at the 300 kV test accelerator. At the second beam line of the test accelerator, a RFQ-postaccelerator (radio frequency quadrupole) is installed which accelerates mA ion beams up to 45 keV/u parameters of the different beam lines available at GSI for implantation experiments are summarized. With this equipment high dose implantation of heavy ions in depths of ~ μ m is possible. Experiments by external research groups started in 1987.

⁺ Lit R. Keller et al., Vacuum 36, 833 (1986)

**An Investigation on Plasma Assisted Plating
System for Thin Film Engineering**

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ABSTRACT

A new arrangement used for plasma assisted vapor deposition processes has been developed. It can combine with any evaporation such as resistive heating, flash evaporation, arc evaporation, rf or induction heating. In the case of a negative substrate bias, the substrate is continuously bombarded by ions extracted from plasma. The plating material was heated and evaporated by an electron beam. Vapor of the material was intensively ionized in the plasma region. The layers of metals, alloys and composition are deposited on silica glass, steel, S.S. in Ar and N_2 or CH_4 . The filament of ion source is made of LaB_6 . So the thermionic emitting of electron was intensified at the low pressure and the properties of ion plated coatings can be improved by increasing the specimen ion current density and operating at low deposition pressure. The uniformity of thickness can be improved by using a target of different potential. The arrangement can also be used for plasma sputtering by an unbalance magnetron.

**The use of cross-sectional transmission electron microscopy
- XTEM -
for depth selective microstructural analysis of implanted metals.**

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A technique has been developed for preparing cross-sectional TEM samples of implanted metal surfaces. Unlike conventional TEM, which makes use of samples parallel to the implanted surface, this XTEM-technique permits a depth selective microstructural study over the entire range of the implanted ions.

A striking observation by XTEM on implanted surfaces of copper and stainless steel is the occurrence of a deep damage layer at depths R_d much larger than the calculated LSS ion range R_p . The ratio R_d / R_p is found to be dependent on:

1. The crystallographic orientation of the ion beam. In copper implanted with 170 keV Al ions R_d / R_p can be as large as 10 for implantations along a (110)-axis, whereas this value is still about 5 for off-axis (random) implantations.
2. The energy E_0 of the ions. For implantations along a (110)-axis R_d is found to increase as the square root of the energy.
3. The ratio S_n / S_e of nuclear and electronic stopping powers. R_d / R_p increases with increasing value of S_n / S_e .

From these observations it is concluded that the damage range R_d is determined by the range of channeled ions. Channeling can be reduced but not avoided by random orientation of the ion beam. This is confirmed by simulations using the computer code MARLOWE, which takes channeling into account.

The effect of increasing ion dose on the damage range indicates that the large compressive stress in the top layer is a driving force for the formation of the deep damage.

XTEM on noble gas implanted stainless steel reveals a layer of gas bubbles. The extremely high pressure in these bubbles induces an fcc --> bcc phase transformation in the surface layer as observed by Mossbauer spectroscopy, RBS/channeling and XTEM. The thickness of this martensite layer again corresponds to the range of channeled ions as determined by MARLOWE simulation.

HIGH CURRENT DENSITY, BROAD BEAM ION IMPLANTATION
by
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The capabilities and operating characteristics of the broad beam (10 cm dia), high current density (up to 1500 μ A/cm²) gaseous ion implanter designed and built at Colorado State University will be described briefly. Data showing that large surfaces can be implanted with nitrogen at current densities over 100 times those associated with typical commercial implanters to produce high quality implanted layers without inducing detrimental effects on typical subsurface bulk materials will be presented. Definitive evidence, obtained using a unique oscillating pin-on-rotating disc wear tester, that implanted nitrogen does not migrate significantly when it is subjected to typical sliding wear conditions will be presented. Comparative wear data obtained using a stationary pin-on-rotating disc machine will be used to show why data obtained using this conventional wear test equipment erroneously suggests that nitrogen migrates during the wear process. Preliminary performance data obtained on the broad beam, high current density metal ion implanter currently under development will be presented.

A NEW MACHINE FOR COMBINED PHYSICAL VAPOR DEPOSITION
AND ION IMPLANTATION OF THIN FILMS

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In this paper the design and preliminary performance data of a new machine which allows the formation of complex ion beam assisted coatings are described.

The apparatus consists of a Duoplasmatron ion source, a mass analyzer, a target chamber adaptable for use with various samples up to 10 cm in diameter, and a 2 crucible electron gun evaporator equipped with film thickness monitor. It was conceived with a high degree of process automation.

The hybrid technique combines some of the better features of both deposition, co-deposition and implantation to produce surface alloy layers with a high control of microstructure and properties. Homogeneity of the formed films and their adherence to the substrate are highly improved with respect to those of samples obtained by conventional implantation or deposition alone.

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